PCB Concentrations in Fishes from the Housatonic River, Connecticut, 1984–2010, and in Benthic Insects, 1978–2010

Final Report

Report No. 11-04F

Prepared for the

General Electric Company

by the

Patrick Center for Environmental Research
The Academy of Natural Sciences of Philadelphia
1900 Benjamin Franklin Parkway
Philadelphia, Pennsylvania 19103-1195

November 3, 2011

GE
159 Plastics Avenue
Pittsfield, MA 01201
USA

November 9, 2011

Ms. Susan Peterson
Connecticut Department of Energy and Environmental Protection
Water Management Bureau
79 Elm Street
Hartford, CT 06106

Mr. Dean Tagliaferro
U.S. Environmental Protection Agency
c/o Weston Solutions, Inc.
10 Lyman Street
Pittsfield, MA 01201

Re: Housatonic River, Connecticut
Report on 2010 Fish Sampling and Benthic Insect Sampling

Dear Ms. Peterson and Mr. Tagliaferro:

Enclosed is a report entitled *PCB Concentrations in Fishes from the Housatonic River, Connecticut, 1984-2010, and in Benthic Insects, 1978-2010*, which was prepared on behalf of the General Electric Company (GE) by the Academy of Natural Sciences of Philadelphia. This report presents the results of the Academy's 2010 fish sampling and benthic insect sampling in the Housatonic River in Connecticut, and it includes comparisons of those results to the results from prior fish and benthic insect monitoring studies.

We would be glad to discuss this report with you. Please let me know if you have any questions or would like additional copies.

Very truly yours,

Kevin Mooney

Kevin Mooney
Project Manager

Enclosure

cc: Susan Svirsky, EPA
Timothy Conway, EPA

Holly Inglis, EPA
Rose Howell, EPA (cover letter and CD of report)
John Looney, CT AG
Brian Toal, CDPH
William Hyatt, CDEEP
Michael Gorski, MDEP (cover letter and CD of report)
Eva Tor, MDEP (cover letter and CD of report)
John Ziegler, MDEP
Linda Palmieri, Weston
Andrew Silfer, GE
Michael Carroll, GE (cover letter only)
Roderic McLaren, GE (cover letter only)
Richard Horwitz, ANSP (cover letter only)
Kevin Russell, Anchor QEA
Stuart Messur, Arcadis
James Bieke, Goodwin Procter
Jeffrey Porter, Mintz Levin
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EXECUTIVE SUMMARY

The Academy of Natural Sciences of Philadelphia (Academy) has conducted biennial fish surveys in the Connecticut portion of the Housatonic River since 1984. Benthic insects were monitored by the Connecticut Department of Environmental Protection (CTDEP) during 1978–1990 and have been monitored by the Academy since 1992. Data for both groups of organisms have documented a clear reduction in PCB concentrations in the biotic component of the river ecosystem since monitoring began.

Results of the Academy's 1994 study indicated a substantial reduction in PCB concentrations in brown trout, smallmouth bass, and benthic insects compared to 1992. Concentrations observed in the 1996–2008 studies were roughly similar to those in 1994 and, for fish, remained well below the levels in 1986–1992. For benthic insects, concentrations in the more recent years (2001-2008) were among the lowest observed since monitoring began.

The 1994 biological monitoring study was the last of the biennial studies required by the 1990 Housatonic River Cooperative Agreement between CTDEP and the General Electric Company (GE). The 1996 and 1998 studies were conducted in order to determine whether the marked reduction in PCB concentrations observed in 1994 had persisted, and the results indicated that it largely had. A new Housatonic River Follow-up Cooperative Agreement was executed by GE and CTDEP in October 1999, requiring continuation of these biennial studies in 2000, 2002, and 2004. Although no cooperative agreement was in effect requiring monitoring in 2006, 2008, or 2010, the biennial monitoring program was nevertheless continued in these years, using the same study design as in previous years. The present report details results from the 2010 fish and benthic insect sampling.

Purpose of Study

The main purpose of the 2010 study was to compare PCB concentrations in brown trout, smallmouth bass, and benthic insects with levels observed in previous study years, and to compare PCB concentrations in smallmouth bass collected at four monitoring stations in 2010.

Sampling Stations

Sampling stations for this biological monitoring study were the same as in previous years. In upstream to downstream order, these were West Cornwall, Bulls Bridge, Lake Lillinonah, and Lake Zoar (see map in Fig. 1 of the report). An additional station (Falls Village, upstream of West Cornwall) was employed, at CTDEP's request, for supplemental sampling that was not part of the biennial monitoring program.

Taxa Monitored

The taxa sampled for long-term monitoring purposes were the same as in the 2000, 2002, 2004, 2006 and 2008 studies and included fish and benthic insects. The fish species were brown trout (collected only at West Cornwall) and smallmouth bass (collected at West Cornwall, Bulls Bridge, Lake Lillinonah, and Lake Zoar). The benthic insect taxa (collected only at West Cornwall) consisted of filter-feeding caddisflies, predatory stoneflies, and predatory dobsonflies. In addition, at CTDEP's request, supplemental samples of northern pike, bluegill, and yellow perch were collected (from Falls Village, Bulls Bridge, Lake Lillinonah, and Lake Zoar) and analyzed for total PCBs. All fish and benthic insect samples were collected during June, August, and October 2010.

PCB Analysis

Analytical Method

PCB analysis was based on the method of Mullin (1985), which allows specific quantitation of over 100 individual PCB congeners. This method permits both congener-based and Aroclor-based determinations of total PCB.

Quantitation of Total PCB

Total PCB was quantified by two procedures. The congener-based procedure sums the concentrations of all individual congeners (up to 121) quantitated by the analytical method. The Aroclor-based procedure is based instead on the concentrations of a much smaller number of congeners that are essentially unique to Aroclor 1254 or 1260. It extrapolates from these marker congeners to Aroclor concentrations, based on the relative proportions of the markers in each Aroclor, and then sums the two Aroclor concentrations. Only the Aroclor-based procedure was used in the 1984–1990 studies, while both methods were used in the 1992–2010 studies.

Data Analysis and Rationale

Two basic types of differences in PCB concentrations are of interest in this study: differences among years and differences among stations. Year differences were assessed for both smallmouth bass and brown trout, using appropriate statistical techniques (see below). Station differences were assessed only for smallmouth bass, since it was the only species monitored at all sampling stations.

PCB concentrations in an individual fish can be influenced strongly by its age (or duration of exposure, which differs from age in fish that are stocked), sex, and lipid content. Since samples collected in different years or at different stations typically differ in their age, sex, and lipid distributions, observed differences in PCB concentrations among years or stations may simply reflect differences in these ancillary variables (e.g., unusually high lipid levels in a particular year) rather than real differences in PCB exposure. At the opposite extreme, real differences in exposure (e.g., a declining trend among years) may be masked by variability created by differences in these ancillary variables. Therefore, to the extent that inferences regarding differences in PCB exposure are of interest, it is important to identify and remove any statistically significant influence of these ancillary variables.

Given these facts, two criteria are paramount in choosing an appropriate statistical technique for analysis of the fish data: it must permit assessment of among-year and among-station variation, and it must permit detection and removal of the effects of differences in ancillary variables (age, sex, lipid content). Analysis of covariance is a standard technique that satisfies both of these requirements, and it was therefore chosen as the basis for assessing the statistical significance of variation among stations and years for the fish data. These statistical assessments have been done by performing pairwise comparisons of covariate-adjusted mean values among stations or among stations. The results of these comparisons are presented in the main body of the text.

While these pairwise comparisons are appropriate, their use for testing among-year differences results in a loss of statistical power as additional years are included in the analysis. As discussed in Appendix L to this report, the large number of pairwise comparisons increases the frequency of spurious significant differences, and the statistical techniques designed to control that frequency reduce statistical power as well.

An alternate approach to testing significance of temporal trends by pairwise comparisons is presented and discussed in Appendix L. This approach, based on the linear contrast method, involves defining and testing a smaller number of *a priori* comparisons of interest. These comparisons involve contrasting the average data from the three most recent years (the 2006, 2008, and 2010 surveys) with those of different periods which have been shown to have had different mean PCB concentrations. These periods are 1984-1986, a period of intermediate PCB concentrations; 1988-1992, a period of higher PCB concentrations; and 1994-2004, a period of lower PCB concentrations immediately preceding the three most recent years. These contrasts provide a useful method of assessing temporal patterns of changes in PCB concentrations.

In contrast, tolerance limits for human consumption of fish and criteria for fish consumption advisories are based simply on the total PCB concentration of a fish fillet (on a wet weight basis). Data for these purposes are therefore reported without adjusting for the effects of ancillary variables.

Results

Comparison of Fish Results with Previous Years

Overall, PCB concentrations in smallmouth bass and brown trout in 2010 were similar to than those found in 1994–2008, and remained well below the levels found in 1992 and most prior years. This pattern held for both Aroclor-based total PCBs (TPCB) and congener-based total PCBs (CTPCB).

For smallmouth bass, there was an apparent pattern of low TPCB concentrations during 1994–2010 compared to 1992 and earlier. Similarly, CTPCB concentrations (which are only available for 1992–2010) appeared lower during 1994–2010 than in 1992. These patterns were confirmed statistically for both TPCB and CTPCB using analysis of covariance and pairwise comparisons between years. While statistical analysis revealed some differences in temporal patterns among stations, they generally confirmed that the concentrations in 2010 were similar to those during 1994-2008, and that the concentrations in those years were significantly lower than those during 1988-1992. For example, for data with all stations combined, the adjusted mean TPCB and CTPCB concentrations for 2010 showed no statistically significant differences from those in any year during 1994–2008 (except for a significant decrease in TPCB compared to 1998), but showed a significant reduction from 1988-1992 (for TPCB) or 1992 (for CTPCB). Similarly, when stations were assessed individually, adjusted mean TPCB concentrations in 2010 at the three upstream stations (West Cornwall, Bulls Bridge, and Lake Lillinonah) were generally not significantly different from those in the years during 1994–2008 (with a few exceptions in which they were lower); and the concentrations in each year during 1994-2010 were generally significantly lower than those in the years during 1988-1992 (with a few exceptions in which they were not significantly different). However, at Lake Zoar, TPCB concentrations in 2010 were not significantly different from those in any of the prior years, including 1988-1992 (except that they were significantly higher than those in 2000).

The results of the linear contrasts approach are generally consistent with the above results. That method found that the TPCB and CTPCB concentrations at West Cornwall, Bulls Bridge, and Lake Lillinonah in the three most recent years (2006-2010) were not significantly different from the concentrations at those stations in 1994-2004 (except for a weakly significant decrease in CTPCB only at Lake Lillinonah). TPCB concentrations in 2006-2010 were significantly lower than those in the 1988-1992 period at these three stations and were significantly lower than those in the 1984-1986 period at Bulls Bridge and Lake Lillinonah.

The data from Lake Zoar show a different pattern in the most recent years, especially 2010. These data show a small increase in smallmouth bass wet-weight PCB concentrations in the three most recent sampling years relative to the immediately preceding years. Similarly, the linear contrasts approach found that, at Lake Zoar, TPCB and CTPCB concentrations in 2006-2010 were significantly higher than concentrations in 1994-2004, but lower than concentrations in 1988-1992 and not significantly different from concentrations in 1984-1986. The cause of the apparent recent increase at Lake Zoar is not known.

For brown trout, TPCB and CTPCB concentrations in 2010 were lower than or similar to concentrations in most years during 1994–2008, and well below levels observed in 1992. This pattern was generally confirmed by analysis of covariance with pairwise comparisons between years. These comparisons showed that TPCB concentrations in 2010 were significantly lower than those in 2008, 2004, and 1984-1992, and not significantly different from those in 1994-2002 and 2006, and that TPCB concentrations in each year during 1994–2010 were significantly lower than those in each year during

1986–1992. Pairwise comparisons of CTPCB concentrations revealed a generally similar pattern.

The results of the linear contrast approach are consistent with those discussed above. That approach found that TPCB and CTPCB concentrations in the three most recent years (2006-2010) were not significantly different from those in the 1994-2002 period, but were significantly lower than those in the 1988-1992 and 1984-1986 periods for TPCB and those in 1992 for CTPCB. (CTPCB data are not available for 1984-1986.)

Comparison of Fish Results among Stations

Visual inspection of the 2010 TPCB and CTPCB data for smallmouth bass indicates higher wet-weight concentrations at West Cornwall and Lake Zoar than at Bulls Bridge and Lake Lillinonah (although lipid-normalized TPCB concentrations were very similar at all stations). Concentrations adjusted for covariates (age, lipid content of fish) showed a similar pattern This differs from previous years when smallmouth bass from the two upstream stations (West Cornwall and Bulls Bridge) had higher concentrations than fish from the two downstream stations (Lake Lillinonah and Lake Zoar). However, using analysis of covariance of data from all years, results showed that TPCB and CTPCB concentrations were significantly higher at the two upstream stations than those at the Lake Lillinonah, which, in turn, were significantly higher than those at Lake Zoar.

Fish Exceeding the FDA Fish Consumption Tolerance Limit

For comparison with previous Housatonic River biological monitoring studies, an assessment was made of the percentage of fish with fillet PCB concentrations exceeding the U.S. Food and Drug Administration (FDA) fish consumption tolerance limit of 2.0 mg/kg wet weight. None of the 40 smallmouth bass samples in 2010 had CTPCB concentrations exceeding the FDA limit, and 2 of 40 (5%), all from Lake Zoar, had TPCB concentrations exceeding that level. Among brown trout, 7 of 30 fish (23%) had CTPCB and TPCB concentrations exceeding the FDA limit. The percentages of smallmouth bass and brown trout with concentrations *below* the FDA limit were generally similar to those in the 1994-2008 period (with some variations in both directions), and were substantially higher than most of the percentages observed during 1984–1992.

Supplemental Fish Sampling Results

In addition to the biennial monitoring program, GE agreed to collect and analyze an additional 12 northern pike (as 12 individual samples), 40 yellow perch (as eight five-fish composite samples), and 20 bluegill (as four five-fish composite samples) . Of the northern pike samples, six specimens (three from Falls Village, two from Bulls Bridge, and one from Lake Zoar) had TPCB concentrations greater than the FDA fish consumption tolerance limit, and three of them (all from Falls Village) also had CTPCB concentrations above the limit. All yellow perch and bluegill samples had TPCB and CTPCB concentrations below the FDA tolerance limit.

Benthic Insect Results

Analysis of benthic insect samples showed that: (a) PCB concentrations in predatory stoneflies in 2010 were similar to those in 1998–2008; (b) concentrations in filter-feeding caddisflies were similar to those in 1998–2005 and 2008 and somewhat lower than those in 2006; and (c) concentrations in predatory dobsonflies were similar to those in 2006 and 2008, higher than those in 2002 and 2005, and lower than those in 1998 and 2001. Concentrations in all three taxa in 2010 were considerably lower than those in 1992–1996. Rank correlation analysis of the entire data series for 1978–2010 revealed a highly statistically significant temporal trend of decreasing PCB concentrations in both filter feeders and predators.

Conclusions

Results of the 2010 fish monitoring study show that total PCB concentrations in brown trout and smallmouth bass were generally similar to those observed in the 1994–2008 studies (except for an anomalous increase in smallmouth bass concentrations in Lake Zoar), and were well below the levels observed in 1992 and most prior years. Similar patterns hold for both filter-feeding and predatory benthic insects, which also show a highly statistically significant temporal trend of decreasing total PCB concentration over the monitoring period (1978–2010). These findings indicate that the substantial reduction in PCB content of fish and benthic insects that occurred after the 1992 study and was seen in the 1994–2008 studies has persisted into 2010.

QUALITY ASSURANCE STATEMENT

Study Number:601

Study Title: PCB Concentrations in Fishes From the Housatonic River, Connecticut, 1984–2010, and in Benthic Insects, 1978–2010.

This study was performed under the general provisions of the Patrick Center's Quality Assurance Implementation Plan (Rev. 1, June 1998). The final report has been determined to be an accurate reflection of the data obtained.

The dates that Quality Assurance activities on this study were completed are given below.

Data Reviews: Fisheries 26 August 2011
Chemistry 6 September 2011
Insects 27 July 2011
Report Review 6 September 2011

Archiving: Raw data and the final report are filed in the Patrick Center's archives.

Robin S. Davis

Robin S. Davis
Quality Assurance Unit
Patrick Center for Environmental Research
Academy of Natural Sciences

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INTRODUCTION

The Academy of Natural Sciences of Philadelphia (Academy) has conducted biennial fish surveys in the Connecticut portion of the Housatonic River since 1984 (ANSP 1995, 1997, 1999, 2001, 2003, 2005, 2007, 2009). Benthic insects were monitored by the Connecticut Department of Environmental Protection (CTDEP) during 1978–1990 and have been monitored by the Academy since 1992. Data for both groups of organisms have documented a clear reduction in PCB concentrations in the biotic component of the river ecosystem since monitoring began.

Results of the Academy's 1994 study indicated a substantial reduction in PCB concentrations in brown trout, smallmouth bass, and benthic insects compared to 1992. Concentrations observed in the 1996–2008 studies were roughly similar to those in 1994 and, for fish, remained well below the levels for 1986–1992. For benthic insects, concentrations in the more recent years (2001, 2002, 2005, 2006, 2008) were among the lowest observed since monitoring began.

The 1994 biological monitoring study was the last of the biennial studies required by the 1990 Housatonic River Cooperative Agreement between CTDEP and the General Electric Company (GE). The 1996 and 1998 studies were conducted in order to determine whether the marked reduction in PCB concentrations observed in 1994 had persisted, and the results indicated that it largely had. A new Housatonic River Follow-up Cooperative Agreement was executed by GE and CTDEP in October 1999, requiring continuation of these biennial studies in 2000, 2002, and 2004. Although no cooperative agreement was in effect requiring monitoring in 2006, 2008, and 2010, the biennial monitoring program was nevertheless continued in these years, using the same study design as in previous years. The present report details results from the 2010 fish and benthic insect sampling.

The main objectives of the 2010 study were the following:

- *Measure PCB concentrations in selected Housatonic River fish.* As a continuation of prior studies, the species sampled and analyzed for total PCBs were brown trout at West Cornwall and smallmouth bass at West Cornwall, Bulls Bridge, Lake Lillinonah, and Lake Zoar (sampling locations are shown in Fig. 1). In addition, at CTDEP's request, supplemental samples of northern pike, bluegill, and yellow perch were collected (from Falls Village, Bulls Bridge, Lake Lillinonah, and Lake Zoar) and analyzed for total PCBs.

- *Measure PCB concentrations in selected benthic insects at West Cornwall.* As a continuation of prior studies, the insect taxa sampled and analyzed for total PCBs were filter-feeding caddisflies, predatory stoneflies, and predatory dobsonflies.

- *Compare PCB concentrations measured in brown trout and smallmouth bass with concentrations measured in previous years, and compare PCB concentrations measured in smallmouth bass spatially across the four stations sampled.*

- *Compare measured PCB concentrations for each benthic insect group with those measured in previous years.*

For maximum comparability with previous results, fish samples employed in the monitoring study were collected from the same locations and during the same primary seasonal time period as in prior years. The number of brown trout collected at West Cornwall and the number of smallmouth bass collected at all four stations were comparable to the numbers collected in the 1994, 1998, 2000, 2002, 2004, 2006, and 2008 studies and were greater than the numbers collected in 1996 (when the numbers of specimens were reduced at CTDEP's request). An attempt was also made to ensure that the size distribution of fish collected was generally consistent with previous studies.

The remainder of the text of this report describes study methods, summarizes the data, and presents the results of statistical analyses for species that are part of the long-term monitoring program (brown trout, smallmouth bass, and benthic insects). Supporting information is provided in appendices. Sampling methods and PCB data for the supplemental samples of northern pike, bluegill, and yellow perch are detailed separately in Appendix K.

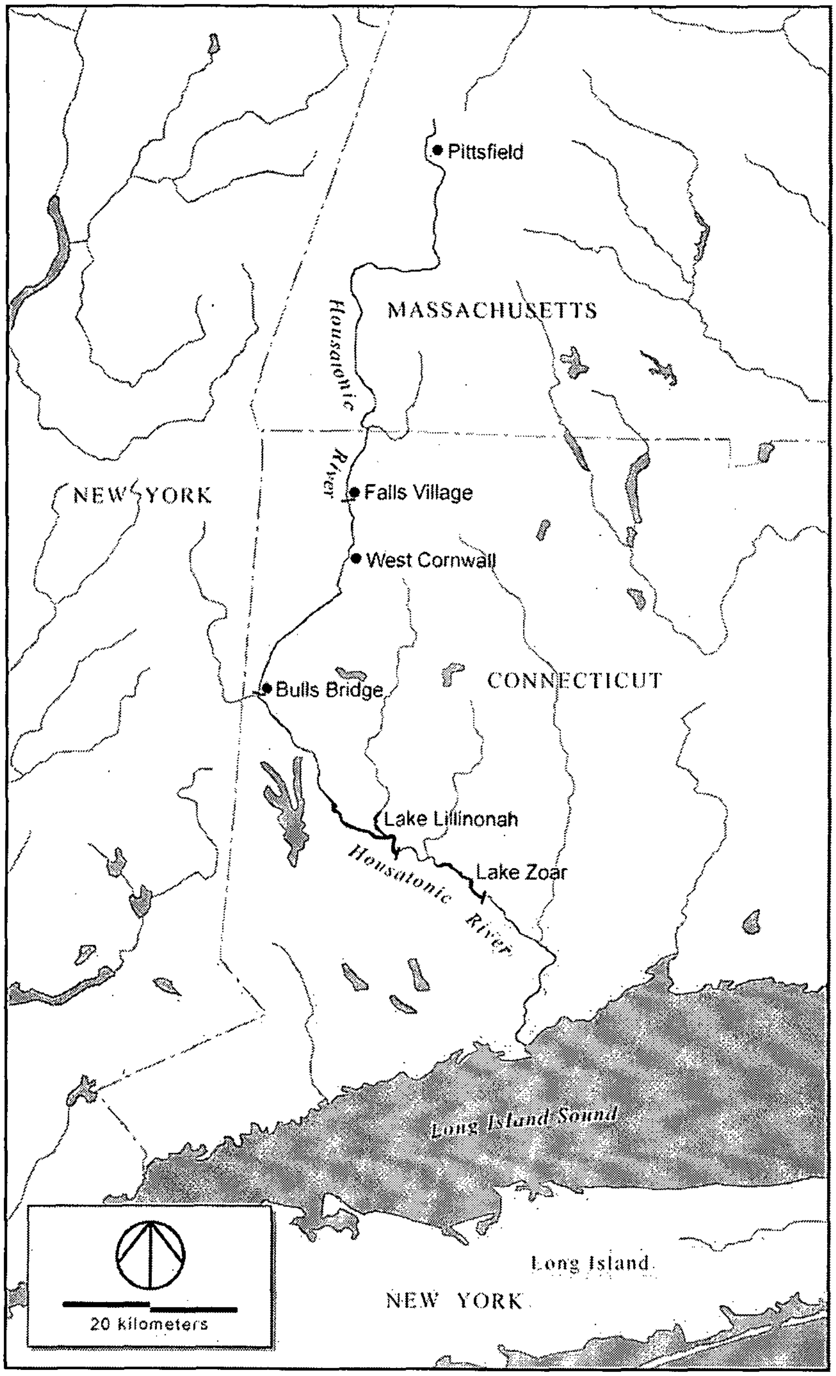

Figure 1. Map of the Housatonic River showing sampling stations for the 2010 fish and benthic insect collections in Connecticut. Smallmouth bass were collected at West Cornwall, Bulls Bridge, Lake Lillinonah, and Lake Zoar. Brown trout and benthic insects were collected only at West Cornwall. Supplemental samples of northern pike, yellow perch, and bluegill were collected at Falls Village, Bulls Bridge, Lake Lillinonah, and Lake Zoar. Approximate locations of dams at Falls Village, Bulls Bridge, Lake Lillinonah, and Lake Zoar are indicated by bars across the river.

SAMPLING DATES AND LOCATIONS

Fish and benthic insects employed in the monitoring study were collected from the same stations sampled in previous years. In upstream to downstream order, these are West Cornwall, Bulls Bridge, Lake Lillinonah, and Lake Zoar (Fig. 1). As in previous Academy studies, brown trout were collected only at West Cornwall, while smallmouth bass were collected at all four stations. One fish-sampling trip was made by Academy personnel in August 2010 to collect fish from all four stations. In addition, during this visit, certain fish specimens from West Cornwall were provided to the Academy by CTDEP personnel. A second fish-sampling trip to Lake Zoar was made by the Academy in October 2010. Table 1 summarizes fish collection dates and techniques for the four sampling stations employed in the monitoring study.

TABLE 1. Summary of fish sampling dates, methods, and locations for fish collections on the Housatonic River, Connecticut, in 2010. Symbols: BS = boat electrofishing, WS = walk-along (shore) electrofishing. ** denotes collection of some fish by CTDEP personnel

Sampling Location	Sampling Dates in 2010		
	9-10 Aug	11-12 Aug	19-Oct
West Cornwall	WS**		-
Bulls Bridge	BS	-	-
Lake Lillinonah	-	BS	-
Lake Zoar	-	BS	BS

West Cornwall

Holdover brown trout, 2010-stocked brown trout, and smallmouth bass were collected from several locations (including Turnip Island, and Furnace Brook Refuge) at the West Cornwall station and Housatonic River Trout Management Area on 9 August 2010 by CTDEP personnel using walk-along shocking equipment. Additional sampling was conducted on 10 August 2010 by Academy personnel using walk-along shocking at the "Garbage Hole," 0.5 km downstream from the Covered Bridge at West Cornwall.

Benthic insect samples were collected by Academy personnel on 23 and 24 June, 2010 within the riffle upstream from the County Road 128 bridge and upstream of Mill Brook at West Cornwall (upstream of the Covered Bridge). This is the same site that was sampled in the 2004, 2006, and 2008 studies.

Bulls Bridge

Fish were collected by Academy personnel at Bulls Bridge on 10 August 2010 by boat electrofishing. Boat electrofishing was conducted during the afternoon throughout the entire station, which extended from about 0.5 km above the State Route 341 bridge at the Kent School to an area 1.7 km downstream of the State Rt. 341 bridge.

Lake Lillinonah

Fish were collected by Academy personnel at the Lake Lillinonah station by boat electrofishing on 11 August 2010 in the morning and on 12 August in the early afternoon. Boat electrofishing was conducted in inlets or coves, around docks, and along rocky ledges and shorelines. Sampling was conducted from about 5.0 km below State Route 133 bridge to 5.0 km above State Route 133.

Lake Zoar

Fish were collected by Academy personnel at the upper end of Lake Zoar (both banks) by boat electrofishing on 11 August 2010 and again on 19 October 2010. The lower end of the reservoir (mainly left bank) was sampled by boat electrofishing on 12 August 2010. Typical habitat sampled by shocking included coves, rock ledges, tree/brush snags, boat docks, and bridge pilings. Sampling in the upper end was conducted just downstream of the Shepaug Dam. Sampling for fish in the lower section of the reservoir was conducted starting at Eichler Cove Marina.

METHODS

Fish Collection and Handling

Brown trout and smallmouth bass were collected by Academy staff, with the assistance of the CTDEP Western Division Fisheries (West Cornwall only), by walk-along and boat electrofishing. Two brown trout from the Burlington fish hatchery were provided by CTDEP for use in determining pre-stocking PCB levels. Table 2 shows the number of specimens of each species collected from each location.

TABLE 2. Number of specimens of each fish species collected from the Housatonic River in 2010 and analyzed for PCBs as part of the long-term monitoring program.

Species	Station					Total
	West Cornwall	Bulls Bridge	Lake Lillinonah	Lake Zoar	Burlington Hatchery	
Brown trout	30	-	-	-	2	32
Smallmouth bass	10	10	10	10	-	40
Total	40	10	10	10	2	72

All sampling stations except West Cornwall were sampled using a 17-ft electrofishing boat. A Smith-Root model 5.0 GPP electrofisher controller powered by a 5000 W generator was operated at pulsed DC output within the following ranges, depending on site and conditions: 180–250 volts, 20% pulse width, 80–100 pulses/sec, and 8–11 amps. Most boat electrofishing was conducted in the morning and early afternoon. A Robin generator and Coffelt VVP unit operated at AC output fitted in a canoe was provided by CTDEP and was used for walk-along (tow-barge) electrofishing during daylight hours at West Cornwall.

During boat electrofishing, two persons collected the stunned fish with long-handled dip nets, while the boat operator controlled the boat and the electrical output of the shocker. Specimens were held in river water in a pre-cleaned metal tub (washed with Micro-90® cleaner and rinsed with river water for each location). Target specimens were identified and measured to ensure collection of appropriately sized fishes. The fish were then placed in a clean stainless steel pan (Micro-90® washed and river water rinsed for each location) that was set on wet ice inside a cooler. Samples were processed within 1 to 6 h from the time of capture. Specimens not required for chemical analysis were measured and released alive.

In addition to boat electrofishing, fish were collected with a walk-along electrofishing unit. While walk-along electrofishing, two operators carried an anode pole connected to a hoop covered with fine mesh (to aid in collecting stunned fish) and a mesh dip-net. The operators and one additional netter collected the stunned fish and placed them in a five-gallon bucket of river water until they were identified and processed after the sampling effort was completed.

Two hatchery trout were provided by CTDEP. In 2010, these fish were taken from the Burlington hatchery in October, as in the 2000 study. In the 2002, 2004, 2006, and 2008 studies, fish were taken from the Burlington hatchery in August, concurrent with the August trout sampling trip. Hatchery fish were previously taken in August (1994–1998 studies) and May (1986 and 1988 studies), depending on availability of hatchery fish. In previous studies, PCB concentrations in hatchery fish have been uniformly low regardless of collection date.

At the field processing site, fish specimens required for chemical analysis were measured for total length to the nearest 0.1 cm with a standard metal ruler affixed to a pre-cleaned measuring board. Each specimen was assigned a unique field serial number, which was attached to the package containing the specimen and recorded in the field notes. Specimens were wrapped individually in clean, muffled aluminum foil. Fish were individually marked with a Floy tag inserted into the head of specimens. The outside of each foil pack was labeled with an index card bearing information on date of capture, species, locality of capture, and serial number. The foil pack and index card were secured with freezer tape and stored on dry ice in clean coolers (Micro-90® washed). Specimens were maintained frozen on dry ice and transported to the Academy's Philadelphia laboratories. Chain-of-custody forms were prepared in the field and accompanied samples to Philadelphia; they were also used to verify transfer of specimens from state collecting crews to Academy field personnel.

Upon arrival at the Academy's laboratories in Philadelphia, sample data were entered into the Fisheries Section database, and specimens were placed in freezers until laboratory processing. Chain-of-custody forms were used to track samples from Academy field personnel to fisheries laboratory personnel, and then to Academy chemistry laboratory personnel for processing or storage.

Fishes were handled in both the field and lab according to Academy Standard Operating Procedure P-14-04 (Fish Preservation, Fixation, and Curation, Rev. 2) and quality control procedures. Specimens were prepared using clean equipment, and contact between specimens or with uncleaned laboratory surfaces was avoided to minimize chances of contamination.

Benthic Insect Collection and Handling

Benthic insects were collected by rapidly lifting rocks and picking specimens from their surfaces with forceps (perlid stoneflies, hydropsychid caddisflies, and corydalid dobsonflies). Some dobsonflies were collected by backpack electrofishing in numerous 1-m^2 areas within the riffle upstream of the County Road 128 bridge. Each backpack sampling effort was conducted in an upstream to downstream direction with a 1/8-in mesh seine held in place at the downstream end of the area to collect insects.

Benthic insect samples were placed in I-Chem Superfund Analyzed glass jars bearing a label on the outside. At the field site, sample jars were placed on ice in a cooler as they were filled. Samples were then frozen for transport to the Academy's Philadelphia laboratories. Upon arrival, samples were transferred to a freezer and stored frozen until preparation for PCB analysis.

Preparation of Fillet Samples

Fishes to be analyzed for PCBs were partially thawed, after which total length (± 0.1 cm) and weight (± 0.1 g) were measured and identifications were confirmed. Brown trout from West Cornwall were examined for fin clips, and observed marks were recorded. Marks have been used to distinguish among the various size classes of trout that are stocked in a given year: fingerling, yearling, and adult. During sample preparation, external and internal anomalies, presence of parasites, etc. were noted. Laboratory methods followed Academy Standard Operating Procedure P-14-12 (Preparation of Fish Samples for Contaminant Analysis). Lengths measured in the lab were used in all analyses. When possible, sex of specimens was determined by gross macroscopic examination. Each fish was given a four-digit analysis number prefixed by "F–" (e.g., F–0538) that was used for tracking the fillet through chemical analyses.

A cleaned glass filleting plate and a cleaned and rinsed stainless steel fillet knife or scalpel blade were used for each specimen. Prior to filleting the fish, excess mucous and debris were rinsed from the fish with deionized water and/or wiped with a Kimwipe®. Following standard practice based on typical human food-preparation customs, skin and scales were left on trout fillets, while smallmouth bass fillets were prepared with scales removed but skin retained. The left fillet was used for chemical analysis. Fillet weight was recorded and otoliths from all target specimens were removed and preserved in 95% ethanol for subsequent age analysis. The entire fillet (including the flesh covering the abdominal cavity) was minced and placed into pre-cleaned 2000-class jars. The fillets were transferred to the Academy Chemistry Section along with a chain-of-custody form. The remains were wrapped in aluminum foil, labeled, and refrozen, permitting examination or analysis of additional material, if necessary.

Cleaning of the glass plates and fillet knives at the end of each laboratory session included the following steps:

1. Wash with dilute Micro-90® cleaner and thoroughly rinse in deionized water.
2. Rinse in acetone and hexane, and then rinse with dichloromethane and air dry.
3. Cover plate and knife with muffled aluminum foil to avoid contamination prior to use.

Fish Aging

Ages of fish were estimated using otoliths, which are ear-bones found in the brain of fish. Comparison of otolith annuli (year) counts with total lengths and known stocking dates helped in verifying ages of some brown trout. CTDEP stocks brown trout in the Housatonic River in the Trout Management Area (TMA) at West Cornwall. For stocked brown trout, the time of residence in the river (river age) is more meaningful than total age for assessing exposure to PCBs. The brown trout collected in 2010 included yearling and adult fish stocked from the Burlington hatchery in 2010, and adult fish stoked in 2009. In 2010, two sizes of fish were stocked in spring (about 20.3cm and 26.7cm total length), and larger fish were stocked in the fall of 2009 (30.5-35.5 cm total length).

No trout collected in 2010 had any identifying marks to distinguish when they were stocked. Otoliths were the primary method of determining the year of stocking (for both fish stocked in 2010 and holdover trout stocked in earlier years). Otolith bands are irregularly formed in the hatchery, but typical banding patterns are evident in fish after stocking. Thus, hatchery fish had a dark central area with irregular banding corresponding to time in the hatchery, with a distal clear area produced after stocking. Holdover fish had one or more annuli, allowing assessment of stocking year. Fish size and otolith banding were used to discriminate between holdover fish stocked in the spring and fall. For example, larger 2009-stocked fish corresponded to the larger, fall-stocked fish, while smaller 2009-stocked fish corresponded to one of the two smaller size groups stocked in the spring of 2009. As a result, among 2009-stocked fish, larger fish had a lower river-age. Discrimination of the age (size) at stocking is complicated by differential growth rates after stocking. Errors in assignment of fish to these two groups would not affect the primary analysis, since that analysis is based on length of time in river after stocking. In most past studies, holdover trout have been distinguished principally by marks (fin clips and/or elastomer dye marks) and length. In the 1984–2002 studies, the largest non-holdover trout was 33.6 cm total length (lab measurement), while the smallest holdover trout was 32.7 cm, so there is a small overlap in lengths.

The largest pair of otoliths (sagitta) was dissected from the fish in the laboratory during the filleting procedure and placed in small vials of 95% ethanol. One of the sagitta was embedded with fast-cure epoxy resin and dried. Thin transverse sections were cut through the otolith with a Buehler Isomet low-speed saw. Three to five of these thin sections per fish were affixed to a microscope slide with immersion oil. Sections were examined under a dissecting microscope at 12–50x magnification. Specimens that were more difficult to age were examined under a compound microscope (50–400x magnification). Digital images of otolith sections were also taken. These were generally adequate for aging, especially for bass, but image quality and single focus of images complicated aging from images.

When viewing sectioned otoliths, annuli (annual marks) are visible as pronounced dark bands, containing within them thin, faint bands representing other cycles of growth. Age was estimated by counting the pronounced bands, with the innermost band assumed to represent the first winter-spring transition (between age 0+ and 1+). Ages were determined independently by two fisheries biologists who read the otoliths and compared results. Exact agreement occurred for 95% of the smallmouth bass and 87% of the brown trout. A mutually agreed upon determination was reached for discrepancies in age after re-examining the otolith sections.

Analysis of PCBs

The method of PCB analysis was identical to that employed in the 2002, 2004, 2006, and 2008 studies. The laboratory method used for treatment of fish is based on the Academy's Standard Operating Procedure P-16-77, "Extraction and Cleanup of Fish Tissue for PCB and Pesticide Analysis" (Appendix A), with one exception. Congener 178 was not quantitated in the 2002-2010 analyses. Congener 178 typically occurs as a very small proportion of PCBs in samples, and the exclusion of this congener has essentially no effect on estimates of concentrations total PCBs. Fish tissues and insect samples were ground using a Tissuemizer®, and the homogenized samples were stored frozen until extraction for PCBs. Samples were thawed and 5 g of the homogenate was sub-sampled using a stainless steel spatula. Approximately 30 g of Na_2SO_4 (manufactured by J.T. Baker, previously muffled at 450°C for 4 hours) was added to the sub-sample to eliminate water. The dried sample was placed in a Soxhlet extractor with pre-cleaned glass wool and extracted in a 1:1 hexane-acetone (manufactured by J.T. Baker, pesticide residue grade) mixture for a minimum of 18 h. The extracts were sub-sampled for gravimetric lipid determination. For this, a known volume of the 1:1 hexane-acetone extract was transferred to a pre-weighed aluminum pan. The solvent was evaporated in a fume hood for at least 24 h. The residue remaining (lipid) was weighed and percent lipid was calculated (wet weight basis).

Lipids were removed from sample extracts by treatment with concentrated trace metal grade sulfuric acid (manufactured by J.T. Baker). The organic phase was further cleaned by solid-liquid chromatography using florisil sep-pak columns (manufactured by Burdick and Jackson). The PCBs were eluted from this column using pesticide residue grade hexane.

PCB identification was congener-specific, based on the Academy's Standard Operating Procedure P-16-84 Rev. 2, "Quantification of Individual Polychlorinated Biphenyl Congeners (PCBs), Chlorinated Pesticides and Industrial Compounds by Capillary Column Gas Chromatography" (Appendix B). Congener-specific PCBs were analyzed using a Hewlett Packard 6890 gas chromatograph equipped with a ^{63}Ni electron capture detector and a 5% phenylmethyl silicon capillary column. The identification and quantification of PCB congeners followed the '610 Method' in which the identities and concentrations of each congener in a mixed Aroclor standard (25:18:18 mixture of Aroclors 1232, 1248, and 1262) were determined by calibration with individual PCB congener standards. Congener identities in the sample extracts were based on their chromatographic retention times relative to the internal standards added. In cases where two or more congeners could not be chromatographically resolved, the combined concentrations were reported.

Statistical Methods

Measures of PCB Concentrations

The primary analytical measure used for summarizing and analyzing data was total PCB concentration on a wet weight basis. Total PCB concentration was estimated by two methods. The first was based on measuring the concentrations of selected congeners that are essentially unique to Aroclor 1254 and 1260, extrapolating to Aroclor concentrations from the relative proportions of these congeners in each Aroclor, and then summing the two Aroclor concentrations. The resulting estimate of Aroclor-based total PCB concentration is denoted TPCB. The second measure was calculated by summing concentrations of all of the identifiable PCB congeners. The resulting estimate of congener-based total PCB concentration is denoted CTPCB.

The TPCB method was the only one used in the 1984–1990 monitoring studies, while both TPCB and CTPCB methods were used in the 1992–2010 studies. In a previous study, the two estimates of total PCB were compared using the 1992, 1994, and 1996 data and were found to be highly correlated in all three years (ANSP 1997). This correlation was confirmed by regression analysis of the relationship between the TPCB and CTPCB data for 2010 (Appendix C). Thus, CTPCB is a good surrogate measure for TPCB. In analyses that included all monitoring years, only TPCB was used, while analyses that included only years 1992–2010 were conducted using CTPCB values, since CTPCB values are expected to provide a more accurate measure of total PCB concentrations than do TPCB values. This procedure is consistent with previous monitoring reports.

Variables that Influence PCB Uptake and Retention

PCB concentrations in fishes can be influenced by a variety of factors other than a fish's level of exposure. Influential variables include a fish's river age, lipid content, and sex.

The river age of a fish is the time the fish has spent in the river. For stocked brown trout in the Housatonic River, PCB exposure occurs primarily in the river rather than the hatchery. Therefore, river age is a more meaningful indicator of exposure than is total age. For smallmouth bass, which are not stocked, river age is identical to total age.

Since PCBs partition preferentially into lipid, a fish's PCB uptake rate and steady-state burden are likely to be influenced by its lipid content. Lipid content often differs between sexes, with females having higher lipid levels than males.

Sexes often differ in PCB concentration, presumably because of the loss of PCBs associated with lipid in eggs. Since brown trout do not routinely reproduce in the study area, this mechanism is not expected to occur in trout. Furthermore, sex was not recorded for many trout in earlier studies. Therefore, statistical models of PCB concentrations in brown trout did not use sex as a factor.

Statistical Analyses

One of the major goals of this study was to assess differences in PCB concentrations among years and stations. Because the composition of samples collected in different years or at different stations unavoidably differs somewhat with respect to variables that influence PCB uptake (e.g., river age, lipid content, and sex), differences among samples with respect to these variables could produce statistically significant year or station effects that are not caused by differences in PCB exposure. At the opposite extreme, differences with respect to these variables could mask the effects of real differences in PCB exposure. It is therefore desirable to identify and remove the effects of these confounding variables when they are statistically significant.

Analysis of covariance (ANCOVA), as implemented by the General Linear Model (GLM) procedure in Statistica, was the primary statistical technique used for year and station comparisons. Year, sex, and station were incorporated in ANCOVA models as discrete effects for bass analyses. Only year was incorporated as a discrete effect for trout analyses as trout were only collected at West Cornwall and sex was not expected to affect PCB concentrations. River age and lipid content (both log-transformed) were incorporated as covariates. Statistical significance of effects and covariates was assessed by the p value associated with the F value of the corresponding Type III sum of squares[1] (the Type III sum of squares is discussed in SAS 1985). The statistical significance of variation among years, among stations, and among treatment interactions was assessed.

Statistical distributions of TPCB and CTPCB were strongly positively skewed and thus were inappropriate for analyses that assume a normal distribution, such as ANCOVA. Therefore, following standard statistical practice (e.g., Sokal and Rohlf 1969), TPCB and CTPCB data were log-transformed prior to statistical analysis. The purpose of this transformation is to produce variables whose variance is independent of the mean (homogeneous variance) and whose variation about the mean is approximately normally distributed (Gaussian residuals). These properties are important in ensuring the validity of standard statistical methods such as ANCOVA. Additionally, for positively skewed data, the geometric mean is known to be a better measure of central tendency than is the arithmetic mean and therefore was used in graphical presentations of data.

ANCOVA was used to test for statistically significant differences among stations and years for smallmouth bass and brown trout. Models were designed to examine among-year differences at West Cornwall for brown trout and to examine both among-year and among-station differences for smallmouth bass. ANCOVAs included main effects (station, year, and sex), covariates (log river age and log lipid, where "lipid" is percent lipid on a wet-weight basis), and interaction terms for main effects and covariates. Following standard statistical practice, covariates that were not statistically significant were dropped from the model, and the ANCOVA was repeated to assess significant effects and interactions. With regard to lipid-normalization, this means that PCB levels were adjusted (or normalized) for associated lipid levels in the final model only when ANCOVA indicated that PCB concentrations were influenced significantly by lipid content.

The removal of non-significant terms from a statistical model pools variance associated with the removed effects with residual error. Because this procedure increases both the sums of squares and degrees of freedom of the residual error, it can either increase or decrease the mean squares error. An alpha level of 0.05 was used to remove non-significant terms (Sokal and Rohlf 1969); this pooling did not greatly affect significance of other effects in the analyses performed. In general, once significant main effects were included in models, the significance of interactions did not depend on which other interaction terms were included (e.g., significance of a station-year interaction did not depend on inclusion of station-sex, year-sex, or lipid-station interactions, although they did depend on the inclusion of year and station main effects).

Least-squares means associated with each treatment level were examined to determine differences among mean total PCB levels. The least-squares mean adjusts for covariate effects and thus provides an estimate of PCB content independent of river age, sex, and lipid content (or other influential variables). When probability levels generated from an ANCOVA indicated a

1 Using the Type III sums of squares assesses the contribution of each effect after all other effects in the model have been incorporated.

significant station or year effect, pairwise multiple comparisons were used to identify significant differences between pairs of least-squares means, using the Tukey unequal sample size HSD (honest significant difference) criterion. Thus, any differences detected by these tests represented differences in PCB concentration after accounting for the effects of age, sex, and lipid content.

These pairwise multiple comparisons, in which a separate test is done for each pair of years, have been used throughout the many years of these surveys. This was an appropriate procedure for comparing least-squares means, especially in earlier years when the temporal pattern of concentrations was unclear and no *a priori* hypotheses could be defined. However, as discussed in Appendix L to this report, the use of these pairwise comparisons for testing among-year differences results in a loss of statistical power as additional years are included in the analysis. The large number of pairwise comparisons increases the frequency of spurious significant differences, and the statistical techniques designed to control that frequency themselves reduce statistical power as well.

An alternate approach to testing the significance of temporal trends is presented and discussed in Appendix L. This approach involves defining and testing a smaller number of *a priori* comparisons of interest. These comparisons involve contrasting the average data from the three most recent years (in this case, the 2006, 2008, and 2010 surveys) – used in lieu of only the most recent year given the year-to-year variability – with those of different periods which have been shown to have had different mean PCB concentrations. These periods are 1984-1986, a period of intermediate PCB concentrations; 1988-1992, a period of higher PCB concentrations; and 1994-2004, a period of lower PCB concentrations immediately preceding the three most recent years. This approach uses the statistical method of linear contrasts, as described in Appendix L. Linear contrasts between a single year's data (e.g., the most recent) and other periods were not done, because the amount of year-year variability in concentrations would make it difficult to interpret results of such contrasts. These contrasts provide a useful method of assessing temporal patterns of changes in PCB concentrations.

RESULTS

Summary of the 2010 Monitoring Data for Brown Trout and Smallmouth Bass

Thirty brown trout collected from West Cornwall and two brown trout from the Burlington hatchery were analyzed for PCB content (stocking dates are summarized in Appendix D). Of the 30 specimens from West Cornwall, sex could be determined by macroscopic examination for all trout, which consisted of 10 males and 20 females. Forty smallmouth bass from four stations were analyzed for PCB content, including 15 males and 25 females. The (arithmetic) mean and range of CTPCB concentrations and lipid-normalized CTPCB concentrations for the monitoring samples are summarized in Table 3. Hatchery trout had a geometric mean CTPCB level of 0.01 mg/kg (wet) and were not used in the statistical analyses.

TABLE 3. Arithmetic means and ranges of congener-based total PCB estimates (mg/kg wet weight) in brown trout and smallmouth bass collected in 2010. In the "Male/Female" column, the first and second numbers listed for each entry (e.g., 3/11) are the numbers of male and female specimens.

				River Age		CTPCB		CTPCB/LIPID	
Station	#Specimens	Age criteria	Male/Female	Arith Mean	Range	Arith Mean	Range	Arith Mean	Range
Brown trout (*Salmo trutta*)									
West Cornwall	30	all	10/20	0.79	0.33-4.33	1.34	0.45-3.33	39.10	10.7-132.6
West Cornwall	18*	<30 cm	6/12	0.39	0.33-1.33	0.89	0.45-1.29	32.55	10.7-57.1
West Cornwall	10*	30-40cm	4/6	1.13	0.33-2.33	1.95	0.47-3.33	41.77	13.7-83.6
West Cornwall	2*	>40cm	0/2	2.63	0.92-4.33	2.33	1.62-3.03	84.61	36.6-132.6
West Cornwall	20*	age 0+ Spring	6/14	0.33	0.33-0.33	0.86	0.45-1.29	30.20	10.7-57.1
West Cornwall	10*	holdover	4/6	1.69	0.92-4.33	2.31	0.62-3.33	56.88	13.7-132.6
Smallmouth bass (*Micropterus dolomieu*)									
West Cornwall	10	all	5/5	4.3	3-7	0.93	0.53-1.61	41.34	28.8-58.8
Bulls Bridge	10	all	1/9	7.8	4-17	0.55	0.24-1.03	38.60	21.6-65.0
Lake Lillinonah	10	all	6/4	5.9	2-11	0.50	0.10-1.17	48.89	17.3-190.6
Lake Zoar	10	all	3/7	6.2	3-14	0.96	0.12-1.73	72.06	12.4-216.2
Northern pike (*Esox lucius*)									
Falls Village	3	all	3/0	-	-	6.61	2.01-11.57	365.13	251.0-538.3
Bulls Bridge	3	all	3/0	-	-	1.48	0.60-1.95	117.55	43.9-174.2
Lake Lillinonah	3	all	1/2	-	-	1.13	0.82-1.50	72.57	53.5-100.6
Lake Zoar	3	all	1/2	-	-	1.03	0.48-1.64	59.13	30.9-77.7

* These are subsets of the total number of 30 brown trout, grouped by size or river age.

Comparison with Previous Years

Smallmouth bass and brown trout were the primary fish species of interest in the 2010 monitoring study. Comparisons among years were therefore restricted to these two species, excluding hatchery trout. (A tabular comparison of average PCB content in all species of fishes collected in 1984–2010, without adjustment for the influence of covariables, can be found in Appendix E.)

Smallmouth Bass

Visual inspection of sample (geometric) means for smallmouth bass suggests that TPCB concentrations in 2010 at all stations except Lake Zoar were similar to or slightly lower than those in 2000-2008, and that concentrations during 1994–2010 were generally lower than those during 1986–1992 (Fig. 2A; Table 4). The lipid-normalized TPCB data (Fig. 2B) and the CTPCB data (Table 4, 1994–2010 versus 1992) for these stations also suggest that concentrations in 2010 were generally similar to or slightly lower than those in the 1994-2008 period and that the concentrations in 1994-2010 were lower than those in 1992 and (where applicable) prior years. For Lake Zoar, visual inspection of the sample means suggests that wet-weight TPCB and CTPCB concentrations in 2010 were slightly higher than those in 1994-2008, but lower than those in 1992 (though not, where applicable, prior years) (Fig. 2A; Table 4). On a lipid-normalized basis, the mean TPCB concentration at Lake Zoar in 2010 appears similar to those in 1994-2008 (Fig. 2B).

ANCOVA for data with all stations combined detected no statistically significant differences between TPCB concentrations in 2010 and those in 1994-1996 and 2000-2008. However, TPCB concentrations in 2010 were significantly lower than concentrations in 1998 and 1984-1992 (Table 5). For CTPCB, concentrations in 2010 were not significantly different from those in any study year during 1994–2008, but were significantly lower than those in 1992 (Table 5). (Statistically significant main effects, covariates, and interactions in the ANCOVA models are summarized in Appendix F.) Pairwise comparisons of TPCB data show a trend from higher concentrations in 1988–1992 to lower concentrations in the more recent years. Pairwise comparisons of the CTPCB concentration also show the highest concentration in 1992, followed by lower concentrations in more recent years.

When stations were tested separately for differences between years, there was an overall pattern of decrease after 1992, with some differences in the temporal patterns among stations (Table 6). (Statistically significant main effects, covariates, and interactions in the ANCOVA models are summarized in Appendix F.) While visual inspection suggests that wet-weight TPCB concentrations at all stations except Lake Zoar decreased from 2008 to 2010 (Fig. 2A), this apparent pattern was not confirmed by ANCOVA, which detected no significant difference between TPCB concentrations in 2010 and those in 2008 for any station. At West Cornwall, TPCB concentrations in 2010 were not significantly different from those in any study year during 1994–2008 and 1986, and concentrations in each study year during 1994–2010 were significantly different from those in each study year during 1988–1992. At the other three stations, the trend was not as clear, and many of the years overlapped in significant groups. At Bulls Bridge, TPCB concentrations in 2010 were not significantly different from those in 1996-2004 and 2008 (although they were significantly lower than in 2006); and concentrations in 1996-2002 and 2008-2010 were significantly lower than concentrations in 1984 and 1988-1992. At Lake Lillinonah, TPCB concentrations in 2010 were not significantly different from those in any study year during 1994-2008 except for 1998; and concentrations in 2000-2010 were significantly lower than concentrations from 1988-1992 (other years formed intermediate groupings). At Lake Zoar, TPCB concentrations in 2010 were not significantly different from those in any of the prior years (including 1988-1992), except that they were significantly higher than those in 2000.

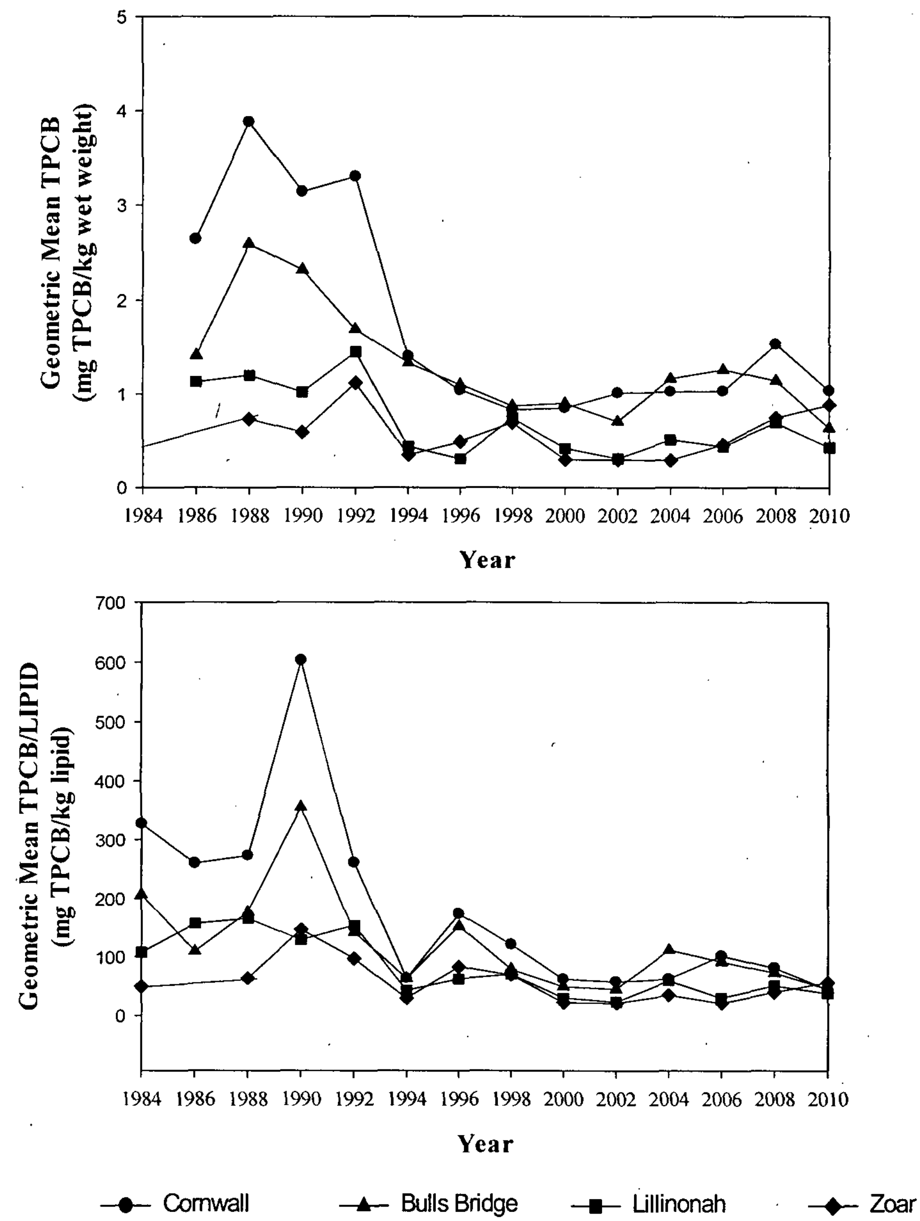

Figure 2. Historical patterns of PCB concentrations in smallmouth bass at four sampling stations on the Housatonic River, 1984–2010. Panel A — Geometric means (unadjusted) of TPCB. Panel B — Geometric means (unadjusted) of lipid-normalized TPCB (TPCB divided by proportion lipid). The pronounced peak in lipid-normalized TPCB in 1990 is due to unusually low lipid levels rather than high TPCB levels (e.g., see Appendix F in ANSP 1995).

TABLE 4. Geometric means (unadjusted) of congener-based total PCB estimates (CTPCB) and Aroclor-based estimates (TPCB) for fish collected in the Housatonic River, CT, 1984–2010.

Year	Brown Trout			Smallmouth Bass			
	Cornwall	Hatchery		Cornwall	Bulls Br	Lillinonah	Zoar
CTPCB							
2010	1.13	0.01		0.88	0.50	0.36	0.74
2008	1.53	0.01		1.26	0.88	0.55	0.62
2006	1.12	0.01		0.83	0.98	0.34	0.37
2004	1.59	0.09		0.88	1.00	0.44	0.25
2002	1.60	0.30		1.04	0.73	0.32	0.31
2000	1.43	0.03		0.86	0.91	0.45	0.27
1998	1.96	0.12		0.72	0.87	0.78	0.69
1996	1.35	–		0.94	0.98	0.28	0.46
1994	1.11	0.42		1.27	1.19	0.41	0.34
1992	6.33	–		2.49	1.29	1.11	0.88
TPCB							
2010	1.32	0.01		1.04	0.63	0.43	0.88
2008	1.82	0.01		1.53	1.14	0.69	0.74
2006	1.40	0.01		1.03	1.26	0.44	0.46
2004	1.85	0.09		1.02	1.16	0.51	0.29
2002	1.55	0.29		1.01	0.71	0.31	0.30
2000	1.41	0.04		0.85	0.90	0.42	0.30
1998	1.93	0.12		0.83	0.87	0.74	0.69
1996	1.41	–		1.04	1.10	0.31	0.49
1994	1.22	0.43		1.40	1.33	0.44	0.35
1992	8.07	–		3.30	1.69	1.45	1.12
1990	5.30	–		3.14	2.32	1.02	0.59
1988	4.80	–		3.88	2.59	1.20	0.73
1986	5.51	–		2.64	1.41	1.13	–
1984	2.30	–		2.00	1.80	1.07	0.39

TABLE 5. Results of smallmouth bass multiple-comparison tests for pairwise differences between least squares means (LSMs) for years or stations, based on the natural logarithm of TPCB for 1984–2010 (excluding 1986) (left column) and the natural logarithm of CTPCB for 1992–2010 (right column) after adjusting for the effects of covariates. Untransformed LSMs can be estimated from the values reported in this table as follows: $y = e^x$, where x is the LSM reported in this table and y is the corresponding untransformed LSM. Years or stations with the same "Group" letter code are not statistically significantly different from one another at $\alpha = 0.05$. These groups are summarized in the bottom table of each column, where years and stations are grouped (with parentheses) from left to right in order of decreasing LSM.

Ln(TPCB)

Year Comparisons

Year	LSM	Group
1984	0.2273	ef
1988	0.5224	fg
1990	0.7604	g
1992	0.5139	fg
1994	-0.3274	cd
1996	-0.3895	bcd
1998	-0.1590	de
2000	-0.8795	a
2002	-0.8485	ab
2004	-0.4027	abcd
2006	-0.3753	cd
2008	-0.4492	abcd
2010	-0.5496	abc

Station Comparisons

Station	LSM	Group
B	0.1502	c
C	0.2494	c
L	-0.3924	b
Z	-0.7324	a

Summary

Effect	Significance Groups
Years	(90 88 92) (88 92 84) (84 98) (98 94 06 96 04 08) (94 06 96 04 08 10) (96 04 08 10 02) (04 08 10 02 00)
Stations	(C B) (L) (Z)

Ln (CTPCB)

Year Comparisons

Year	LSM	Group
-		
-		
-		
1992	0.3104	d
1994	-0.3392	bc
1996	-0.5610	ab
1998	-0.1082	c
2000	-0.6875	a
2002	-0.6998	a
2004	-0.4873	abc
2006	-0.5024	ab
2008	-0.5049	ab
2010	-0.4046	abc

Station Comparisons

Station	LSM	Group
B	-0.1124	c
C	-0.0715	c
L	-0.5765	b
Z	-0.8335	a

Summary

Effect	Significance Groups
Years	(92) (98 94 10 04) (94 10 04 06 08 96) (10 04 06 08 96 00 02)
Stations	(C B) (L) (Z)

TABLE 6. Results of smallmouth bass multiple-comparison tests for pairwise differences between least squares means (LSMs) for years at each sampling station, based on the natural logarithm of TPCB for 1984–2010 (excluding 1986) after adjusting for the effects of covariates (see Table 8 for the corresponding untransformed LSMs). Years or stations with the same "Group" letter code are not statistically significantly different from one another at $\alpha = 0.05$. These groups are summarized in the bottom table, where years are grouped (with parentheses) from left to right in order of decreasing LSM.

West Cornwall		
Year	LSM	Group
1984	0.8715	bc
1986	0.0693	a
1988	1.4611	d
1990	1.4432	cd
1992	1.3180	cd
1994	0.0798	a
1996	0.3144	ab
1998	0.0771	a
2000	-0.2051	a
2002	-0.2235	a
2004	0.3881	ab
2006	0.2545	ab
2008	0.3078	ab
2010	0.0855	a

Bulls Bridge		
Year	LSM	Group
1984	0.7155	efg
1986	0.3814	cdef
1988	1.0323	gh
1990	1.3920	h
1992	0.7809	fg
1994	0.4217	def
1996	-0.0739	abcd
1998	-0.1467	abc
2000	-0.3808	ab
2002	-0.4881	a
2004	0.1440	bcde
2006	0.3731	cdef
2008	0.1299	abcde
2010	-0.2840	ab

Lake Lillinonah		
Year	LSM	Group
1984	0.0698	cdef
1986	0.0712	def
1988	0.0735	ef
1990	0.2713	f
1992	0.0841	ef
1994	-0.8723	a
1996	-0.5664	abcde
1998	-0.1154	bcdef
2000	-1.0321	a
2002	-1.1500	a
2004	-0.6979	abcd
2006	-0.8485	ab
2008	-0.7882	abc
2010	-0.9631	a

Lake Zoar		
Year	LSM	Group
1984	-0.5344	bcd
1986	-	-
1988	-0.3095	bcd
1990	0.1558	d
1992	-0.1144	cd
1994	-1.2276	ab
1996	-0.5495	bcd
1998	-0.3274	bcd
2000	-1.6121	a
2002	-1.1799	ab
2004	-1.1992	ab
2006	-1.0234	abc
2008	-0.7269	bcd
2010	-0.3447	bcd

TABLE 6 (continued). Results of smallmouth bass multiple-comparison tests for pairwise differences between least squares means (LSMs) for years at each sampling station, based on the natural logarithm of TPCB for 1984–2010 (excluding 1986) after adjusting for the effects of covariates (see Table 8 for the corresponding untransformed LSMs). Years or stations with the same "Group" letter code are not statistically significantly different from one another at $\alpha = 0.05$. These groups are summarized in the bottom table, where years are grouped (with parentheses) from left to right in order of decreasing LSM.

Summary	
Station	Significance Groups*
West Cornwall	(88 90 92) (90 92 84) (84 04 96 08 06) (04 96 08 06 10 94 98 86 00 02)
Bulls Bridge	(90 88) (88 92 84) (92 84 94 86 06) (84 94 86 06 04 08) (94 86 06 04 08 96) (86 06 04 08 96 98) (04 08 96 98 10 00) (08 96 98 10 00 02)
Lake Lillinonah	(90 92 88 86 84 98) (92 88 86 84 98 96) (86 84 98 96 04) (84 98 96 04 08) (98 96 04 08 06) (96 04 08 06 94 10 00 02)
Lake Zoar	(90 92 88 98 10 84 96 08) (92 88 98 10 84 96 08 06) (88 98 10 84 96 08 06 02 04 94) (06 02 04 94 00)
*Listed in order of decreasing LSM	

The results of the analyses of linear contrasts (Appendix L) are generally consistent with the above results, although linear contrasts often found more clear-cut differences. At West Cornwall, the TPCB and CTPCB concentrations in the three most recent years (2006-2010) were not significantly different from those in 1994-2004 and 1984-1986, but were significantly lower than those in the 1988-1992 period. At Bulls Bridge, the TPCB and CTPCB concentrations in 2006-2010 were not significantly different from those in 1994-2004, but were significantly lower than those in the 1984-1986 period and those in the 1988-1992 period. At Lake Lillinonah, CTPCB concentrations in 2006-2010 were significantly lower than those in 1994-2004 and those from 1992, while TPCB concentrations in 2006-2010 showed no significant difference from those in 1994-2004, but were significantly lower than those in the 1984-1986 and 1988-1992 periods. At Lake Zoar, TPCB and CTPCB concentrations in 2006-2010 were significantly higher than concentrations in 1994-2004, lower than concentrations in 1988-1992, and not significantly different from concentrations in 1984-1986.

Brown Trout

Visual inspection of sample (geometric) means for brown trout suggests that mean TPCB and CTPCB concentrations in 2010 were similar to or slightly lower than mean concentrations in 1994–2008 and well below the mean concentrations in 1992 (and prior years for TPCB) (Table 4; Fig. 3A for TPCB; Appendix G). The same overall pattern is evident in the lipid-normalized TPCB data (Fig. 3B).

This apparent pattern was generally confirmed by ANCOVA. (Statistically significant main effects, covariates, and interactions in the ANCOVA models are summarized in Appendix F.)

Pairwise comparisons showed that: (a) TPCB concentrations in 2010 were significantly lower than those in 2008, 2004, and 1984-1992, but not significantly different from those in 1994-2002 and 2006; and (b) TPCB concentrations in each study year during 1994–2010 were significantly lower than those in each study year during 1986–1992 (Table 7). Pairwise comparisons of CTPCB concentrations revealed a broadly similar pattern, showing that: (a) CTPCB concentrations in 2010 were significantly lower than in 2004, 1998, and 1992, but not significantly different from those in 1994-1996, 2000-2002, and 2006-2008; and (b) CTPCB concentrations in each year from 1994 through 2010 were significantly lower than those in 1992 (Table 7).

The results of the linear contrast approach (Appendix L) are generally consistent with those discussed above. That approach found no significant differences between TPCB and CTPCB concentrations in the most recent years (2006-2010) and those in the 1994-2004 period. It also found that TPCB concentrations in the most recent years (2006-2010) were significantly lower than those in both the 1984-1986 and the 1988-1992 periods, and that CTPCB concentrations were likewise significantly lower in the most recent years than in 1992.

Comparison among Stations

Visual inspection of mean TPCB and CTPCB concentrations for smallmouth bass in 2010 indicates that wet-weight concentrations appear higher at West Cornwall and Lake Zoar than at

TPCB (TPCB divided by proportion lipid). The pronounced peak in lipid-normalized TPCB in 1990 is due to unusually low lipid levels rather than high TPCB levels (e.g., see Appendix F in ANSP 1995).

Bulls Bridge and Lake Lillinonah (Table 4; Fig. 2A). This differs from previous years, when smallmouth bass from the two upstream stations (West Cornwall and Bulls Bridge) had higher concentrations than fish from the two downstream stations (Lake Lillinonah and Lake Zoar). On a lipid-normalized basis, in 2010, all four locations had virtually the same TPCB concentration per unit lipid (Fig. 2B).

Using a statistical model that included data from all years, analysis of covariance revealed the following statistically significant station differences in mean TPCB and CTPCB concentrations: Pairwise comparisons indicated that, for both CTPCB and TPCB, concentrations at West Cornwall and Bulls Bridge did not differ significantly from each other, and were significantly higher than concentrations in Lake Lillinonah, which, in turn, were significantly higher than concentrations in Lake Zoar (Table 5). Thus, the higher concentrations at Lake Zoar in 2010 were overshadowed by the general pattern of lower concentrations at that station in other years. However, in this model, the least squares mean TPCB and CTPCB concentrations for Lake Zoar in 2010 were higher than the least squares means for 2010 at the other stations.

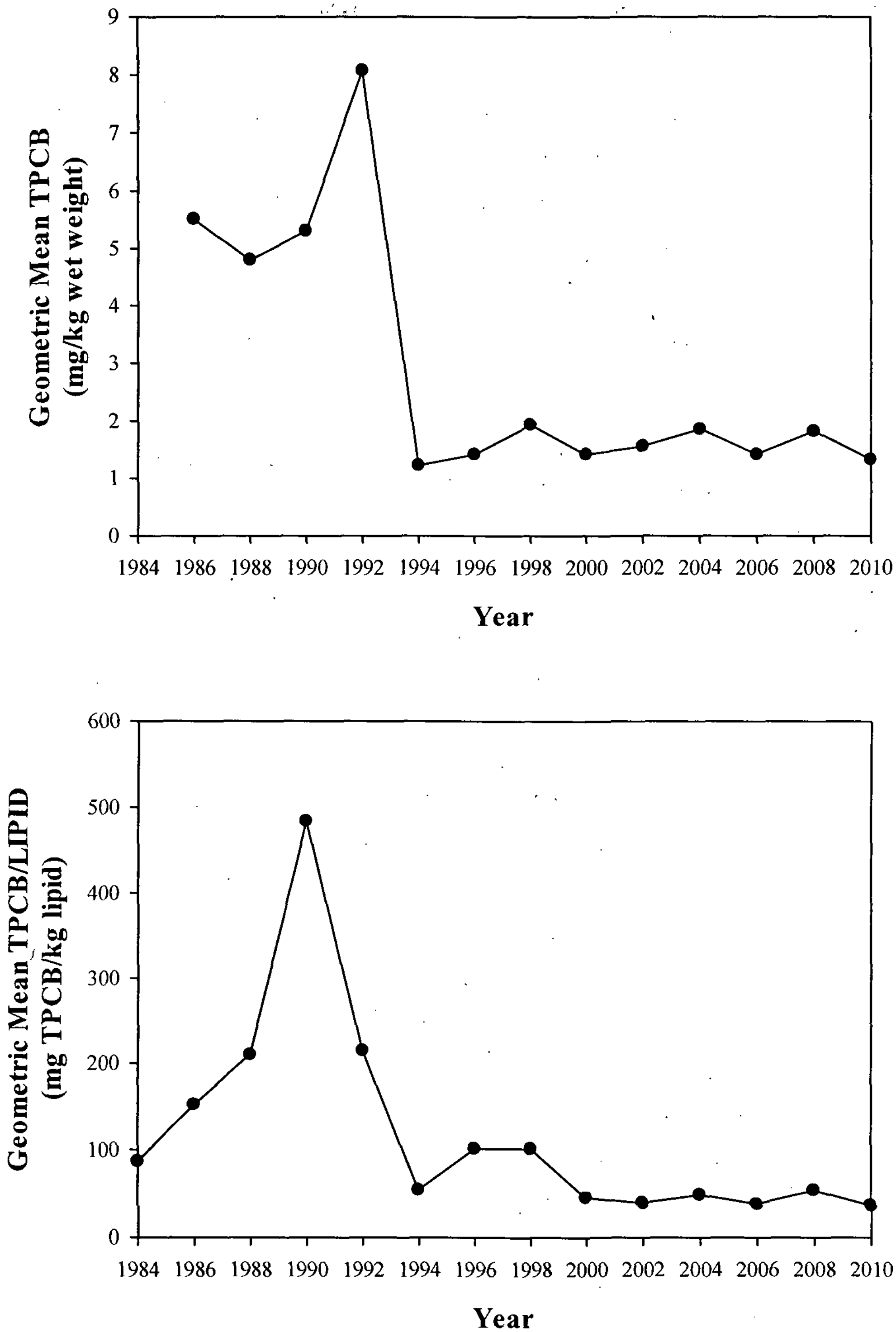

Figure 3. Historical patterns of PCB concentrations in brown trout collected from West Cornwall, 1984–2010. Panel A — Geometric means (unadjusted) of TPCB. Panel B — Geometric means (unadjusted) of lipid-normalized

TABLE 7. Results of brown trout multiple-comparison tests for pairwise differences between least squares means (LSMs) for years at West Cornwall, based on the natural logarithm of TPCB for 1984–2010 (left column) and the natural logarithm of CTPCB for 1992–2010 (right column) after adjusting for the effects of covariates (see Table 8 for the corresponding untransformed LSMs). Years or stations with the same "Group" letter code are not statistically significantly different from one another at $\alpha = 0.05$. These groups are summarized in the bottom table, where years are grouped (with parentheses) from left to right in order of decreasing LSM.

Ln(TPCB)			**Ln(CTPCB)**		
Year	LSM	Group	Year	LSM	Group
1984	0.5181	e	-		
1986	0.9064	f	-		
1988	1.2099	fg	-		
1990	1.5045	gh	-		
1992	1.7243	h	1992	1.8419	d
1994	0.2104	bcde	1994	0.4185	bc
1996	-0.4962	a	1996	-0.2364	a
1998	0.1871	bcde	1998	0.5167	c
2000	0.0145	abcd	2000	0.3188	abc
2002	-0.1409	abc	2002	0.2521	abc
2004	0.2754	cde	2004	0.5153	c
2006	-0.0582	abcd	2006	0.1012	abc
2008	0.3438	de	2008	0.4579	bc
2010	-0.2272	ab	2010	-0.0318	ab

Summary	
Measure	Significance group
Ln(TPCB)	(92 90) (90 88) (88 86) (84 08 04 98 94) (08 04 98 94 06 00) (04 98 94 06 00 02) (98 94 06 00 02 10) (06 00 02 10 96)
Ln(CTPCB)	(92) (98 04 08 94 00 02 06) (08 94 00 02 06 10) (00 02 06 10 96)

TABLE 8. Untransformed least-squares means (LSMs) corresponding to the LSMs of transformed TPCB and CTPCB concentrations shown in Figures 2 and 3 and listed in Tables 6 and 7. Values in this table have units of mg/kg wet weight and are related to those in Figures 2 and 3 and in Tables 6 and 7 as follows: $y = e^x$, where x is a value in Figures 2 and 3 and y is the corresponding value in this table. All smallmouth bass LSMs are for TPCB, while LSMs for both TPCB and CTPCB are presented for brown trout.

Year	2010	2008	2006	2004	2002	2000	1998	1996	1994	1992	1990	1988	1986	1984
Smallmouth bass														
W. Cornwall	1.09	1.17	1.17	0.85	0.69	0.74	1.02	1.34	1.00	3.73	3.75	3.48	2.53	2.35
Bulls Bridge	0.75	0.99	1.34	1.12	0.57	0.57	0.86	0.99	1.44	1.81	3.63	2.63	1.39	2.00
Lillinonah	0.38	0.46	0.44	0.53	0.27	0.31	0.80	0.46	0.64	1.22	1.15	1.09	1.24	1.19
Zoar	0.71	0.49	0.36	0.30	0.29	0.20	0.71	0.59	0.29	0.90	1.15	0.71	0.56	0.50
Brown trout (W. Cornwall)														
TPCB	0.80	1.46	0.95	1.45	0.91	1.04	1.19	0.59	1.22	5.83	4.32	3.27	2.72	1.68
CTPCB	0.97	1.9	1.13	2.08	1.45	1.53	2.01	1.46	1.62	2.24	-	-	-	-

Fish Exceeding the FDA Fish Consumption Tolerance Limit

Previous reports on the Housatonic River biological monitoring studies have included an assessment of the percentage of fish with total PCB concentrations in fillets exceeding the U.S. Food and Drug Administration (FDA) fish consumption tolerance limit of 2.0 mg/kg wet weight. For comparison with those prior assessments, a similar assessment was conducted for fish collected in 2010.

None of the 40 smallmouth bass in 2010 had CTPCB concentrations above the FDA limit (Table 9). Two of those 40 bass (5%) had TPCB concentrations exceeding the limit. Both were caught in upper Lake Zoar and included a 40.5-cm male and a 48.4-cm female. Among brown trout, 7 of 30 samples (23%) had CTPCB and TPCB concentrations exceeding the FDA limit (Table 9). These included five trout (31.4. 31.9, 32.1, 32.4. and 36.0 cm total length) with a river-age of 1.3 years, probably stocked in the spring of 2009 (although possibly stocked in the fall of 2009). Additionally, there were two trout – a 39.4-cm male with a river-age of 2.3 years and a 47.1-cm female with a river-age of 4.3 years – with concentrations greater than 2.0. The 47.1-cm fish was the largest and oldest brown trout collected in the 2010 study.

The percentages of brown trout and smallmouth bass with total PCB concentrations *less* than the FDA limit in each study year are shown in Table 9. The percentage of brown trout with TPCB concentrations less than 2.0 mg/kg wet weight in 2010 was greater than the percentage found in 2008, less than the percentage found in 2006, and similar to percentages found in studies during 1994-2004. The percentages of such trout in 2010 and in the 1994-2008 period were much greater than those in 1986-1992. A similar pattern holds for CTPCB data. For smallmouth bass, the percentage of fish with TPCB concentrations less than 2.0 mg/kg wet weight was relatively low or variable during 1984–1992 and has remained high since 1994, reaching 100% for many years and stations (including 2010, except for TPCB at Lake Zoar).

In addition to the results for brown trout and smallmouth bass samples in the long-term monitoring study, the 2010 study also included 12 supplemental samples of individual northern pike from Falls Village, Bulls Bridge, Lake Lillinonah, and Lake Zoar (3 from each station), as well as eight 5-fish composite samples of yellow perch (2 from each station) and four 5-fish composite samples of bluegill (1 from each station) (see Appendix K). Three of the northern pike, all from Falls Village, had CTPCB and TPCB concentrations greater than the FDA limit of 2.0 mg/kg. Three other pike, 2 from Bulls Bridge and 1 from Lake Zoar, had TPCB concentrations (but not CTPCB concentrations) above the limit. These six fish ranged in size from 72.2 cm to 105.2 cm. All of the yellow perch and bluegill samples had TPCB and CTPCB concentrations below the FDA limit.

TABLE 9. Summary of percentages of brown trout and smallmouth bass at each sampling station with total PCB concentrations less than 2.0 mg/kg wet weight. All percentages except those in parentheses are based on TPCB. Values in parentheses are based on CTPCB (available for years 1992–2010) and are given only where different from those based on TPCB.

Year	Brown Trout	Smallmouth Bass			
	C	C	B	L	Z
2010	77	100	100	100	80 (100)
2008	50 (60)	80 (90)	80 (100)	80 (90)	90
2006	90 (93)	90 (100)	80 (100)	100	90
2004	63 (87)	90 (100)	100	100	100
2002	73 (70)	100	100	100	100
2000	86	100	100	100	100
1998	60	100	100	100	90
1996	60 (70)	100	100	100	100
1994	86 (92)	69 (77)	100	100	100
1992	0 (2)	14 (21)	75 (88)	75 (88)	71
1990	0	17	17	100	100
1988	0	8	21	88	88
1986	4	31	58	77	–
1984	50	38	50	92	100

Benthic Insects

Benthic aquatic insect larvae were collected in the general vicinity of West Cornwall in June 2010 and were analyzed for total PCB and lipid. Three taxonomic groups were sampled: filter-feeding caddisflies (family Hydropsychidae), predatory dobsonflies (family Corydalidae; the aquatic larvae are also known as hellgrammites), and predatory stoneflies (family Perlidae). The amount of material collected in the field was sufficient to permit analysis of two composite samples for each group. The results are summarized in Table 10 and show concentrations in the range of approximately 0.6 to 2.0 mg/kg.

Historical data on total PCB concentrations in Housatonic River benthic insects are shown in Figure 4 (CTPCB) and Figure 5 (TPCB). (The Academy's CTPCB and TPCB data for 1992–2010 are tabulated in Appendix H; TPCB data for years prior to 1992 were provided by CTDEP.) As shown in Figure 4, CTPCB concentrations in stoneflies and caddisflies in 2010 were generally similar to those in 1998–2008, with a few exceptions. For dobsonflies, CTPCB concentrations in 2010 were similar to those in 2006-2008, higher than those in 2002 and 2005, and lower than those in 1998 and 2001. CTPCB concentrations in all three taxa in 2010 were lower than those in 1992–1996.

TABLE 10. PCB and lipid levels in aquatic insects collected from the Housatonic River in the vicinity of West Cornwall in June 2010. CTPCB denotes congener-based total PCB concentrations, while TPCB denotes Aroclor-based total PCB concentrations. Lipid-normalized values are given in units of mg CTPCB or TPCB in wet tissue per kg lipid in wet tissue. Values for all three insect taxa are geometric means of two composite samples (arithmetic means are similar and are not shown).

Taxon	Proportion lipid	Tissue Concentration		Lipid-normalized Concentration	
		CTPCB	TPCB	CTPCB	TPCB
Caddisflies (Hydropsychidae)	0.041	0.67	0.80	16.20	19.36
Dobsonflies (Corydalidae)	0.058	1.63	2.04	28.20	35.32
Stoneflies (Perlidae)	0.031	0.61	0.67	19.74	21.61

The TPCB data allow comparisons with concentrations as early as 1978. After averaging dobsonfly and stonefly concentrations to obtain a single estimate for predators in each year (for consistency with pre-1992 data), TPCB concentrations in both filter feeders and predators in 2010 were similar to the corresponding values in 2001–2008, somewhat lower than those in 1994–1998, and well below most of the values in 1978–1992 (Fig. 5).

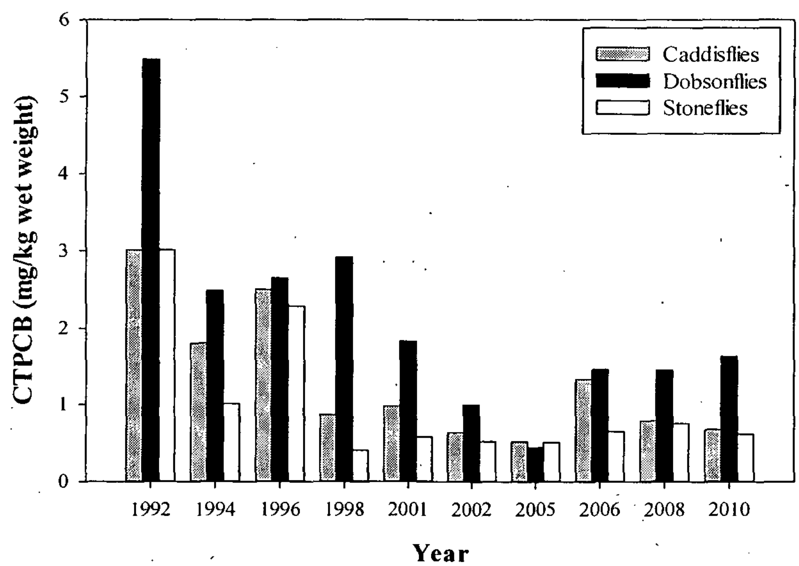

Figure 4. Total congener-based PCB concentrations (CTPCB) in benthic aquatic insects from West Cornwall, 1992–2010. Caddisflies are filter feeders, while dobsonflies and stoneflies are predators. Values are geometric means of two or three composite samples for each group, except in cases where only a single composite sample was analyzed. Plotted values and sample sizes are tabulated in Appendix H.

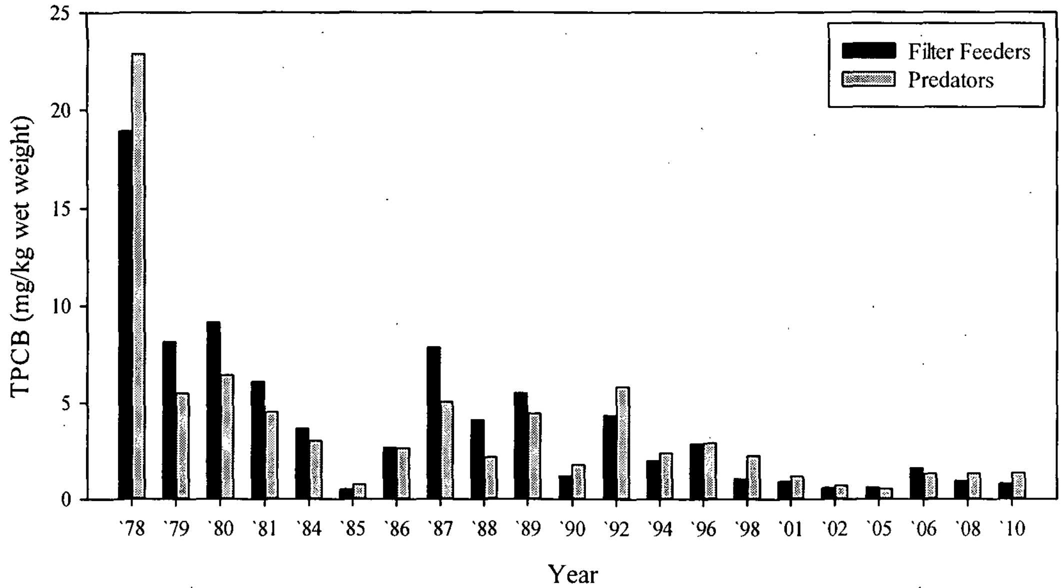

Figure 5. Historical data series of total Aroclor-based PCB concentrations (TPCB) in benthic aquatic insects, 1978-2010. Filter feeders consist of hydropsychid caddisflies, while predators include both dobsonflies and perlid stoneflies. Values for predators are arithmetic means of separate values for dobsonflies and stoneflies.

The historical data series shown in Figure 5 suggests overall decreasing trends in TPCB concentrations in both filter feeders and predators. Kendall's test of rank correlation was used to determine whether there is statistically sound evidence for these apparent trends. The results indicate highly statistically significant decreasing trends in both groups of benthic insects (Table 11).

TABLE 11. Results of Kendall's test of rank correlation between TPCB and study year for filter-feeding and predatory insects, 1978–2010. Reported p values are for one-tailed tests of the null hypothesis that the true correlation is zero, with the alternative hypothesis that the true correlation is negative. Since the same test is applied to two groups, each p value should be compared with Bonferroni-adjusted error rate $\alpha/2 = 0.025$ to ensure an experiment-wise error rate of $\alpha = 0.05$. Note that p is much less than 0.025 for both insect groups, providing strong evidence that the true correlation between TPCB and study year is negative in both cases.

Insect Group	Number of Studies	Correlation Coefficent (Kenall's τ)	p-value
Filter Feeders	21	-0.59	0.00018
Predators	21	-0.54	0.00058

Precision, Accuracy, and Detection Limit Analyses

Methods used to assess precision, accuracy, and detection limits were the same as in the 2002, 2004, 2006, and 2008 studies and are described below.

Detection Limits

Matrix blanks were generated to monitor possible laboratory contamination and to calculate the detection limits for PCBs. (See Appendix I for protocol for detection limit calculations.) Each matrix blank, consisting of approximately 30 g of clean Na_2SO_4, was analyzed using the same procedures as the samples. The detection limit was estimated as the blank area plus three times the standard deviation of the average blank peak areas. The method detection is reported on a mass per mass basis (dividing by an average extraction mass of 5.05 ng). The matrix blank-based detection limits for PCBs (see Appendix J for individual detection limits) ranged from 0.004 ng/g (congener 85) to 8.15 ng/g (congener 3). Based on the matrix blanks, the average detection limit for individual PCB congeners was 0.27 ng/g and that for total PCBs was 22 ng/g (Appendix J). As discussed further below, the calculation of total PCB concentrations for both TPCB and CTPCB excluded sample results that fell below detection limits.

Surrogate Recoveries

Analyte loss through analytical manipulations was assessed by the addition of surrogate PCB congeners 14, 65, and 166 to all samples prior to extraction by Soxhlet apparatus. These surrogates were not industrially prepared and therefore are not present in the environment. Average recoveries of congeners 14, 65, and 166 were 96 ± 7%, 89 ± 6%, and 95 ± 10% respectively. With relatively low standard deviations, constant recoveries regardless of contaminant concentration, and no known interferences, these surrogate congeners are reliable for assessing analyte loss. All reported values for PCB concentration in this study were not corrected for analyte loss.

Duplicate and Triplicate Analyses

Relative percent differences (RPDs) for duplicates were relatively low, with an average (individual congener totals) RPD value of 19%. RSDs (relative standard deviations) for triplicates were also low, with an average (individual congener totals) RSD of 16%. In most instances where RPD and RSD values were high, the associated concentration value was very low, increasing the standard error.

Standard Reference Materials

For this study, National Institute for Standards and Technology (NIST) standard reference materials (SRM 1946, Lake Superior Fish Tissue and SRM 1947 Lake Michigan Fish Tissue) were used to evaluate extraction efficiency and analytical accuracy. For SRM 1946, the average percent recovery was 81% excluding outliers. These outliers (congeners 18, 63, 158, 201 and

206) contribute to only 17% of total SRM congeners quantified and mainly represent uncertified NIST values. The four uncertified congeners excluded from the average value are typically those that represent the lowest concentrations within the SRM matrix. As concentration decreases within a sample, the associated standard error (a measure of the ability to accurately quantify the true concentration) increases. This trend was observed in our evaluation of the SRM concentrations and is typical for PCB analysis. SRM 1947 showed similar results, with an average percent recovery of 81% excluding outliers. For this SRM, outliers (congener 158 and 206) represent less than 7% of total SRM concentrations. Despite the variable recoveries for a small subset of outlier congeners, the overall results of our SRM evaluations denote a high degree of analytical accuracy (Figs. 6 and 7).

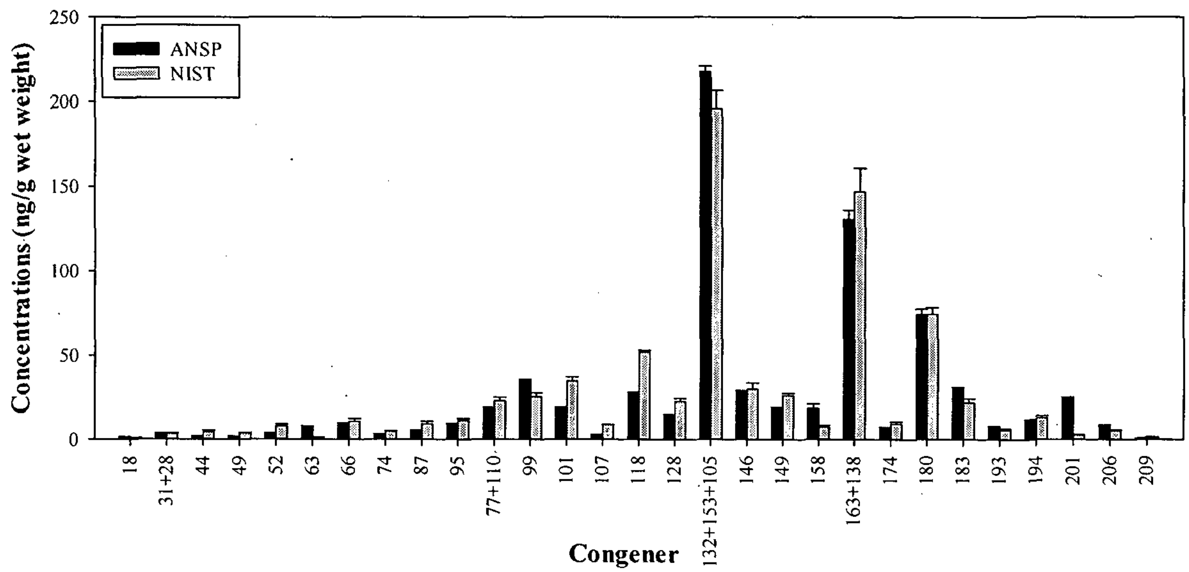

Figure 6. Comparison of 2010 Academy (ANSP) and NIST PCB values for SRM 1946 –Lake Superior fish (error bars denote 1 standard deviation).

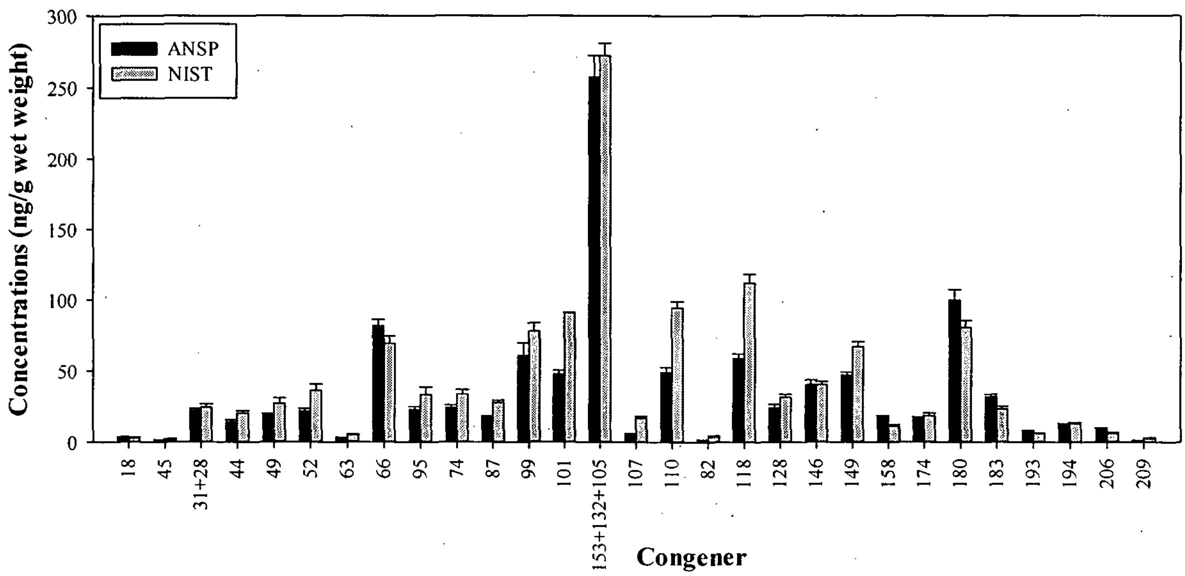

Figure 7. Comparison of ANSP and NIST values for SRM 1947-Lake Michigan fish (error bars denote 1 standard deviation).

Method Spikes

Analyte losses for all PCB congeners were determined through method spikes, using a 25:18:18 mixture of Aroclors 1232, 1248, and 1262 in a blank matrix (one containing no biological matrix). The average percent recovery of spiked congeners was 103%. This average excludes outlier data (PCB congeners 4+10, 29, 131, 158, and 209) because they appear at very low concentrations within the PCB standard used (Mullin, 1985). The average relative standard error for method spikes was +3%.

Combining Congeners

In 2010, as in 2008, concentrations of PCB congeners 31 and 28 were combined and reported as [31+28], and concentrations of congeners 41 and 71 were combined and reported as [41+71], since individual congeners within these two pairs could not be well resolved chromatographically.

Handling of Non-Quantifiable Congeners

Total concentrations of PCBs, as either TPCB (Aroclor-based) or CTPCB (congener-based), are presented in this report. Concentrations of individual congeners and data qualifiers are not reported here, but were reviewed as part of the quality assurance/quality control (QA/QA) procedure. In that review, results for congeners that were not quantifiable were qualified with one of three qualifiers. Congeners that were not detected (no discernible peak arising from the instrument noise) were denoted as "ND". Where a peak was found but the resulting concentration fell below the defined detection limit, "BDL" was used in lieu of reporting the concentration. Congener 84 was not analyzed and was denoted as "NA". All three of these categories of data were excluded from the calculations of total concentrations for both TPCB and CTPCB.

Re-extractions

In an effort to ensure accuracy of results, five fish samples were re-extracted. Two of the five were randomly selected (Chem IDs 5606 and 5607). The replication of these two samples was added to the initial run and treated as a triplicate analysis. These data were included in calculations of the accuracy of quantitation in the QA/QC review.

One sample (Chem ID 5628) was re-extracted due to inconsistent lipid analyses. Although total PCB values remained low, lipid analyses were unusually different. As a result, the sample was essentially run in quadruplicate with the outlier lipid percent removed. In addition, two supplemental fish samples (Chem IDs 5725 and 5729) were selected for re-extraction due to high total PCB values. Results of samples not randomly selected were not incorporated into replicate analyses for the QA/QC review.

DISCUSSION

The results of this study of PCB concentrations in fish and benthic insects in the Connecticut portion of the Housatonic River consist of among-year and among-station comparisons of smallmouth bass at four sampling stations (West Cornwall, Bulls Bridge, Lake Lillinonah, and Lake Zoar), and among-year comparisons of brown trout and benthic insects at a single sampling station (West Cornwall).

Evaluation of Smallmouth Bass Data

For smallmouth bass, there was an apparent pattern of low TPCB concentrations during 1994–2010 compared to 1992 and earlier. Similarly, CTPCB concentrations (which are only available for 1992–2010) appeared lower during 1994–2010 than in 1992. These patterns were confirmed statistically for both TPCB and CTPCB using analysis of covariance and pairwise comparisons between years. Though there were some differences in temporal patterns among stations, statistical analyses generally confirmed that the concentrations in 2010 and other years since 1994 were lower than the concentrations in 1992 and, where applicable, prior years. For data with all stations combined, the adjusted mean TPCB and CTPCB concentrations for 2010 showed no statistically significant differences from those in any year during 1994–2008 (except for a significant decrease in TPCB compared to 1998), but showed a significant reduction from 1988-1992 (for TPCB) or 1992 (for CTPCB).

Similarly, when stations were assessed individually, adjusted mean TPCB concentrations in 2010 at the three upstream stations (West Cornwall, Bulls Bridge, and Lake Lillinonah) were generally not significantly different from those in the years during 1994–2008 (with the exception that they were significantly lower than those at Bulls Bridge in 2006 and Lake Lillinonah in 1998). However, the concentrations in each year during 1994-2010 were generally significantly lower than those in the years during 1988-1992, with a few exceptions (i.e., those at Bulls Bridge in 2006 and Lake Lillinonah in 1996 and 1998 were not significantly different from 1988-1992). However, at Lake Zoar, TPCB concentrations in 2010 were not significantly different from those in any of the prior years, including 1988-1992, except that they were significantly higher than those in 2000.

The results of the linear contrasts approach (Appendix L) are generally consistent with the above results. That method found that the TPCB and CTPCB concentrations at West Cornwall, Bulls Bridge, and Lake Lillinonah in the three most recent years (2006-2010) were not significantly different from the concentrations at those stations in 1994-2004 (except for a marginally significant decrease in CTPCB concentrations at Lake Lillinonah). It also found that the TPCB concentrations in 2006-2010 were significantly lower than those in 1988-1992 period at these three stations and were significantly lower than those in the 1984-1986 period at Bulls Bridge and Lake Lillinonah.

The wet-weight PCB data from Lake Zoar show a different pattern in the most recent years, especially 2010, from the three more upstream stations. These data show a small increase in smallmouth bass PCB concentrations in the three most recent sampling years relative to immediately preceding years, such that concentrations in 2010 at Lake Zoar were slightly higher than those at two upstream stations (Bulls Bridge and Lake Lillinonah), though still lower than those at West Cornwall. Similarly, the linear contrasts approach found that, at Lake Zoar, TPCB and CTPCB concentrations in 2006-2010 were significantly higher than concentrations in 1994-2004, but lower than concentrations in 1988-1992 and not significantly different from concentrations in 1984-1986. The cause of this apparent recent increase at Lake Zoar is not known. On a lipid-normalized basis, the mean TPCB concentration at Lake Zoar in 2010 was similar to those in 1994-2008.

In terms of spatial distribution, the 2010 TPCB and CTPCB data for smallmouth bass indicate higher wet-weight concentrations at West Cornwall and Lake Zoar than at Bulls Bridge and Lake Lillinonah. This differs from previous years when the bass data indicated a pattern of decreasing concentrations from the two upstream stations (West Cornwall and Bulls Bridge) in a downstream direction to Lake Lillinonah and Lake Zoar. However, analysis of covariance of data from all years showed that TPCB and CTPCB concentrations were significantly higher at the two upstream stations than those at the Lake Lillinonah, which, in turn, were significantly higher than those at Lake Zoar. Thus, the higher wet-weight concentrations at Lake Zoar in 2010 were overshadowed by the general pattern of lower concentrations at that station in other years. On a lipid-normalized basis, in 2010, all four locations had virtually the same TPCB concentration.

Evaluation of Brown Trout Data

For brown trout, TPCB and CTPCB concentrations in 2010 appeared lower than or similar to concentrations in most years during 1994–2008, and well below levels observed in 1992. This pattern was generally confirmed by analysis of covariance with pairwise comparisons between years. These comparisons showed that TPCB concentrations in 2010 were significantly lower than those in 2008, 2004, and 1984-1992 and not significantly different from those in 1994-2002 and 2006, and that TPCB concentrations in each year during 1994–2010 were significantly lower than those in each year during 1986–1992. Pairwise comparisons of CTPCB concentrations revealed a generally similar pattern, showing that 2010 concentrations were not significantly different from those in the years during 1992–2008 (except that they were significantly lower than in 1998 and 2004), and that concentrations in each year during 1994-2010 were significantly lower than those in 1992.

The results of the linear contrast approach (Appendix L) are generally consistent with those discussed above. That approach found that TPCB and CTPCB concentrations in the three most recent years (2006-2010) were not significantly different from those in the 1994-2002 period, but were significantly lower than those in the 1988-1992 and 1984-1986 periods for TPCB and those in 1992 for CTPCB (CTPCB data are not available for 1984-1986).

Historical Perspective on Fish Data

Historically, PCB concentrations in fish in the Connecticut portion of the Housatonic River exhibited a pattern of high values in the late 1970s, a substantial decrease around 1980, and subsequently variable behavior at concentrations well below those of the late 1970s (ANSP 1997). After unusually low levels were observed in 1984, higher levels were found in 1986–1992. There was then a substantial decrease in PCB concentrations in 1994, and that decrease has largely persisted in subsequent years through 2010.

Fish Exceeding FDA Fish Consumption Tolerance Limit

A similar temporal pattern is reflected in the percentage of fish with fillet PCB concentrations exceeding the FDA tolerance limit of 2.0 mg/kg wet weight. In the 1984-1992 studies, smallmouth bass with concentrations exceeding that limit were relatively common at most stations, with the exceedance percentage typically being highest at West Cornwall and decreasing downstream. In 1994–1998, smallmouth bass exceeding the limit were rare. In the 2000, 2002, and 2004 studies, none of the smallmouth bass collected from the four stations had a CTPCB concentration exceeding the limit (although one bass in 2004 had a TPCB concentration exceeding that level). In 2006 and 2008, a few of the smallmouth bass (4 of 40 in 2006 and 7 of 40 in 2008) had TPCB concentrations exceeding the limit, with fewer (1 in 2006 and 3 in 2008) also having CTPCB concentrations exceeding the limit. In 2010, no smallmouth bass had CTPCB concentrations above the FDA limit, and two of the 40 fish (5%) (both large individuals from Lake Zoar) had TPCB concentrations greater than the limit.

Among brown trout, nearly all the fish collected from West Cornwall in the years 1986–1992 had PCB concentrations exceeding the FDA limit. Since then, the percentage of trout exceeding the limit has decreased substantially. In the 2006 study, 3 of the 30 specimens from West Cornwall (10%) had TPCB concentrations that exceeded the FDA limit, while only 2 of the specimens (7%) had CTPCB concentrations above the limit. In 2008, 15 of 30 brown trout (50%) had TPCB concentrations exceeding the limit, and 12 of 30 (40%) had CTPCB concentrations exceeding the limit. In 2010, 4 of the 30 specimens (77%) had TPCB and CTPCB concentrations greater than the limit.

In addition, the 2010 study included the supplemental sampling of other fish species from Falls Village, Bulls Bridge, Lake Lillinonah, and Lake Zoar. This effort included the collection and analysis of 12 individual northern pike samples, eight 5-fish composite samples of yellow perch, and four 5-fish composite samples of bluegill. Of the northern pike samples, 6 specimens had TPCB concentrations greater than the FDA limit and 3 of them also had CTPCB concentrations above the limit. These results are roughly similar to those from 2008, when 5 of the 12 northern pike samples had TPCB and CTPCB concentrations above the FDA limit. In 2010, as in 2008, all samples of the smaller fish species (yellow perch and bluegill in 2010, yellow and white perch in 2008) had TPCB and CTPCB concentrations below the FDA tolerance limit.

Evaluation of Benthic Insect Data

Analysis of benthic insect samples showed that: (a) PCB concentrations in predatory stoneflies in 2010 were similar to those in 1998–2008; (b) concentrations in filter-feeding caddisflies were similar to those in 1998–2005 and 2008 but were somewhat lower than those in 2006; and (c) concentrations in predatory dobsonflies were similar to those in 2006 and 2008, somewhat higher than those in 2002 and 2005, and lower than those in 1998 and 2001. Concentrations in all three taxa in 2010 were lower than those in 1992–1996. Rank correlation analysis of the entire data series for 1978–2010 revealed a highly statistically significant temporal trend of decreasing PCB concentrations in both filter feeders and predators. This pattern of PCB concentrations in insects parallels that of fish, decreasing substantially from 1978 through the mid-1980s, increasing to somewhat higher levels in most years between 1986 and 1992, and then decreasing in subsequent years, with some variation among recent years.

Summary

In summary, results of the 2010 Academy of Natural Sciences fish monitoring study show that total PCB concentrations in brown trout and smallmouth bass were generally similar to those observed in the 1994–2008 studies, and were well below the levels observed in 1992 and (where applicable) most prior years. Similar patterns hold for both filter-feeding and predatory benthic insects, which also show a highly statistically significant temporal trend of decreasing total PCB concentration over the monitoring period (1978–2008). These findings indicate that the substantial reduction in PCB content of fish and benthic insects that occurred after the 1992 study and that was seen in the 1994–2008 studies has persisted into 2010.

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APPENDICES

APPENDIX A

SOP No. P-16-77: Extraction and Cleanup of Fish Tissue for PCB and Pesticide Analysis.

ACADEMY OF NATURAL SCIENCES
ENVIRONMENTAL RESEARCH DIVISION

Procedure No. P-16-77
Rev. 2 (9/2011)

EXTRACTION AND CLEANUP OF FISH TISSUE FOR PCB AND PESTICIDE ANALYSIS

Prepared by: Michelle Donnelly and Linda Zaoudeh

Approved by: Robin S. Davis Date: 9/1/2011
Robin S. Davis
Quality Assurance Unit

Procedure No. P-16-77
Rev. 2 (9/2011)

EXTRACTION AND CLEANUP OF FISH TISSUE FOR PCB AND PESTICIDE ANALYSIS

Prerequisite: Use of this method requires a working knowledge of the inherent hazards and possible routes of contamination in working with organic solvents. Also, a working knowledge of glassware cleaning and standard residue analysis techniques is required.

1.0 METHOD

This method includes instructions for extracting PCBs from fish tissue. Also, specific criteria for gas chromatography (ECD-capillary) and quantitation on a congener- and compound-specific basis is included. For basic instructions on gas chromatography, see SOP No. P-16-84.

2.0 SUMMARY

The fish tissue is combined with sodium sulfate, Soxhlet extracted and concentrated to 10 ml. One ml of this extract is taken and analyzed for lipid content. The remainder of the extract is mixed with concentrated acid (to destroy the lipid and other biogenic material) and then cleaned up by Florisil sep-pak chromatography.

3.0 STANDARDS

3.1 PCB Standard

Mixture of Aroclors 1232, 1248 and 1262 in a 25:18:18 ratio. Individual Aroclor concentrations of 250 ng/ml (Aroclor 1232), 180 ng/ml (Aroclor 1248), and 180 ng/ml (Aroclor 1262) are recommended for total PCB concentration of 610 ng/ml.

3.2 Internal Standard

17.5 ng of 2,4,6-trichlorobiphenyl (PCB 30) and 17.5 ng of 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB 204).

3.3 Surrogate Standard

35 ng of 3,5-dichlorobiphenyl (PCB 14), 35 ng of 2,3,5,6-tetrachlorobiphenyl (PCB 65 and 35 ng of 2,3,4,4',5,6-hexachlorobiphenyl (PCB 166).

4.0 APPARATUS

4.1 Glassware (all cleaned using SOP No. P-16-37)

For Extraction: Soxhlet extractors (200 ml), Allihn condensers, 250/500-ml round-bottom flasks.

For Sample Preparation: 250-ml beakers, stainless steel spatula, 10-ml volumetric flasks, Luer lock syringes, 12 ml vials with Teflon-lined screw caps,15ml graduated centrifuge tubes.

4.2 Glass wool for extraction.

4.3 Rotary Evaporator for sample reduction.

4.4 Sodium Sulfate (pre-baked at 450°C).

4.5 Burdick and Jackson Florisil Sep-pak cartridges.

4.6 Sulfuric Acid.

4.7 Tekmar Tissuemizer and Waring Pro Blender.

4.8 Heating mantles and voltage controllers for extraction.

4.9 Teflon boiling chips (pre-extracted overnight in dichloromethane).

5.0 SAMPLE PREPARATION

5.1 Frozen fish fillets are allowed to thaw and are finely ground using the Tekmar Tissuemizer or Waring Blender.

5.2 At the time of analysis, 5 g of thawed fish sample is weighed and placed into a 250-ml beaker. The sample is then combined with sodium sulfate in a 1:6 ratio (sample:sodium sulfate) and mixed with a clean spatula until the sample is homogenized.

5.3 The sample mixture is transferred to a Soxhlet with glass wool at the bottom. At this point the surrogate standard is added. The sample is then extracted overnight (refluxing at least 16 h at 4-6 cycles/h) with 175/350 ml of 1:1 hexane:acetone mixture.

5.4 The extract is reduced to approximately 5 ml using a rotary evaporator, exchanged three times with 25-ml aliquots of hexane, and finally evaporated to 5 ml. Between exchanges the sample is checked for water. If water is present, it is removed with a Pasteur pipet.

5.5 The sample extract is then diluted to 10 ml with hexane using a 15-ml graduated centrifuge tube. The lipid content of the sample is determined at this point by placing a 1.0-ml aliquot of the extract in a pre-weighed aluminum pan. This is allowed to sit at room temperature overnight to dry. The pan is reweighed and the % lipid calculated.

$$\%\,Lipid = \frac{g\,of\,lipid}{total\,sample\,wt.\,(g)} \times 1000$$

5.6 The remaining sample extract is concentrated under a stream of ultra high purity (UHP) nitrogen to approximately 2 ml. It is then washed with an equal volume of sulfuric acid and stored in the refrigerator at 4°C overnight or until separation occurs. In cases where lipid content is high it may be necessary to add more sulfuric acid and hexane. The sample extract is returned to the refrigerator to separate. The hexane phase is transferred to another vial, and the acid phase is washed 2-3 times more with 1-2 ml of hexane, combining all hexane washes. The sample extract (in hexane) is then reduced to approximately 2 ml under a stream of UHP nitrogen.

5.7 The sample extract is cleaned by Florisil column chromatography using Burdick and Jackson sep-pak cartridges. The column is pre-rinsed with approximately 10 ml of hexane which is discarded. The sample is then passed through the column along with three additional rinses of hexane. All deliveries to the sep-pak column are made using a glass Luer-lock syringe. The sample is collected into a 10-ml volumetric flask and the volume adjusted to 10 ml. The sample is now ready for analysis.

6.0 STANDARDS

(For specific volumes and directions see Organic Standards Preparation Logbook.) The following concentrations are recommended based on past GC performance and levels of contaminants typically observed in recent projects.

Working Standards:

PCB Standard: 250 ng/ml of Aroclor 1232, 180 ng/ml of Aroclor 1248, and 180 ng/ml of Aroclor 1262 to yield a total PCB concentration of 610 ng/ml.

Surrogate Standard:

35 ng of 3,5-dichlorobiphenyl (PCB 14), 35 ng of 2,3,5,6-tetrachlorobiphenyl (PCB 65 and 35 ng of 2,3,4,4',5,6-hexachlorobiphenyl (PCB 166).

Internal Standard:

17.5 ng of 2,4,6-trichlorobiphenyl (PCB 30) and 17.5 ng of 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB 204).

7.0 QA/QC

7.1 Laboratory duplicate, laboratory blanks, and standard reference materials (SRMs) are extracted and analyzed at a frequency of 5 to 10% depending on requirements specified by the project documents. Blank spikes are extracted and analyzed at an unspecified frequency to evaluate method performance. Surrogate recoveries provide some measure of method performance for individual sample matrices. Analyte recoveries for SRMs reflect method performance for a variety of compounds in a given type of matrix. SRMs are used in addition to conventional matrix spikes in this procedure.

8.0 AROCLOR QUANTITATION

Aroclor 1254 is quantitated as the sum of congeners 52, 49, 44, 41(+71), 74, 70+76, 95+66, 91, 60+56, 84, 101, 99, 83, 97, 87, 85, 110, 82 divided by 0.5252.

Aroclor 1260 is quantitated as the sum of congeners 178, 187(+182), 183, 185, 174, 177, 171(+202), 172(+197), 180, 170(+190), 201, 203+196 divided by 0.3747.

APPENDIX B

SOP No. P-16-84, Rev. 6: Quantitation of Individual Polychlorinated Biphenyl Congeners (PCBs), Chlorinated Pesticides and Industrial Compounds by Capillary Column Gas Chromatography.

Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S 2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} X_i\right)^2}{n}\right] \quad S = \left(S^2\right)^{\frac{1}{2}}$$

where:

XI; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=l to n.

6. (a) Compute the MDL as follows:

MDL = t(n-1,1-α=0.99) (S)

where:

MDL = the method detection limit

$t(n-1,1-\alpha=.99)$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi.square over degrees of freedom distribution (χ 2 /df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S2 from the current MDL calculation and S2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S2 into the numerator S2A and the other into the denominator S2B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if S2A/S2B<3.05, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if S2A/S2B>3.05, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the Spooled as calculated in 7b to compute The final MDL according to the following equation:

MDL=2.681 (Spooled)

where 2.681 is equal to $t(12,1-\alpha=.99)$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL

UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

Tables of Students' t Values at the 99 Percent Confidence Level

Number of replicates	Degrees of freedom (n-1)	tcn-1,.99)
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title ald the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

[Document accessed via EPA website http://www.epa.gov/epahome/cfr40.htm on 20 June 2005]

APPENDIX C

Relationship Between TPCB (Aroclor-Based) and CTPCB (Congener-Based) Measures of Total PCB Concentration

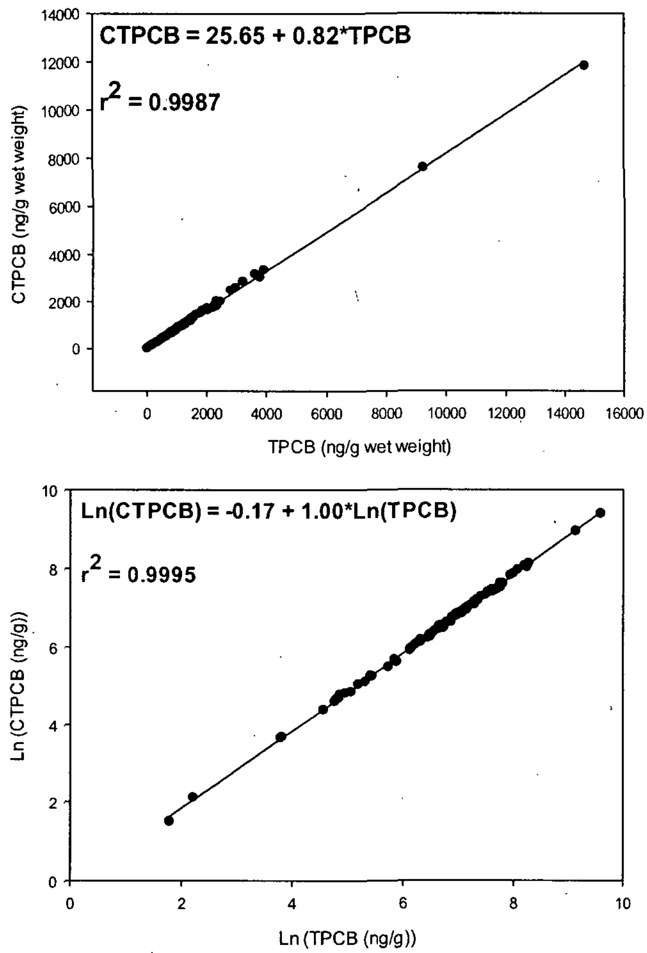

Figure C-1. Relationship between congener-based quantitation of total PCBs and Aroclor-based quantitation for fishes analyzed in the 2010 ANSP Housatonic River study.

As in previous Housatonic River biological monitoring studies, the two methods of quantitating total PCBs were very highly correlated. A scatter plot of 2010 CTPCB concentrations versus the corresponding TPCB concentrations for the fish species analyzed (brown trout, smallmouth bass, northern pike, bluegill, and yellow perch) clearly suggests a linear relationship (Fig. C-1, top). Linear regression analysis of all samples produced an intercept (25.65 ng/g) that differs negligibly from zero, compared to PCB concentrations in this study (regression equation: CTPCB = 25.65 + 0.82*TPCB, r^2=0.9987). The slope of this regression shows that CTPCB was about 82% of TPCB on average. A regression of ln(CTPCB) versus ln(TPCB) was performed to stabilize the variance and check for linearity. The slope of this regression (Fig. C-1, bottom) does not differ from 1.000, indicating a linear relationship.

APPENDIX D

Numbers of Brown Trout from 2010 Analyzed for PCB Content and Their Corresponding Stocking Dates as per Connecticut DEP

Table D-1. The number of brown trout collected and analyzed for PCB content and their corresponding stocking dates. Information on stocking was provided by CTDEP. Fish were assigned to groups based on otolith analysis.

Stocking Date	Number of Individuals	Percent of Total
2010 Spring yearling	8	27
2010 Spring adults	12	40
2009 Fall adult	1	3
Other (2007-2009)	9	30
Total Housatonic	30	100
Burlington Hatchery	2	-

APPENDIX E

Average CTPCB Concentrations in Fish from the Housatonic River, Connecticut

Table E-1. Average CTPCB concentrations in all species of fish collected in the Housatonic River, CT. Results for 1992- 2010 are based on actual quantified CTPCB values. Results for 1984-1990 were estimated from TPCB data, using regressions between LnCTPCB and LnTPCB established with data from 1992 and 1994 (ANSP 1999). C = West Cornwall, B=Bulls Bridge, L=Lake Lillinonah, Z=Lake Zoar, F=Falls Village, HS=Lake Housatonic (only smallmouth bass data presented), H=hatchery.

Species	Station	Mean CTPCB													
		1984	1986	1988	1990	1992	1994	1996	1998	2000	2002	2004	2006	2008	2010
Brown trout	C	2.75	5.27	4.06	4.41	7.25	1.31	2.29	2.29	1.54	1.78	1.64	1.21	1.87	1.26
Rainbow trout	C	-	-	2.63	-	-	-	-	-	-	-	-	-	-	-
Smallmouth bass	C	1.99	2.61	3.77	-	2.78	1.41	1	0.78	1	1.1	0.94	0.89	1.46	0.54
Bluegill	B	0.78	-	1.85	-	-	-	-	-	0.49	-	0.27	-	-	0.48
Brown bullhead	B	0.72	1.54	1.68	-	-	-	-	-	0.34	-	0.37	-	-	-
Common carp	B	0.95	-	5.17	-	-	-	-	-	-	-	-	-	-	-
Largemouth bass	B	1.16	-	2.09	-	-	-	-	-	-	-	0.57	-	-	-
Northern pike	B	-	-	-	-	-	-	-	-	-	-	0.45	0.77	1.74	1.48
Pumpkinseed	B	-	-	0.27	-	-	-	-	-	0.73	-	0.23	-	-	-
Redbreast sunfish	B	1.31	-	1.66	-	-	-	-	0.47	-	-	-	-	-	-
Yellow bullhead	B	-	-	-	-	-	-	-	-	-	-	0.36	-	-	-
Yellow perch	B	1.14	0.72	0.87	0.84	0.56	-	-	0.47	0.27	-	0.36	-	0.36	0.39
Smallmouth bass	B	1.61	1.34	2.33	2.1	1.35	1.23	0.99	0.95	0.98	0.8	1.05	1.08	1.02	0.54
Bluegill	L	0.48	-	0.47	0.47	0.45	-	-	-	-	-	0.17	-	-	0.13
Brown bullhead	L	1.99	-	1.42	-	-	-	-	-	-	-	0.28	-	-	-
Common carp	L	1.85	-	5.61	-	-	-	-	-	-	-	-	-	-	-
Largemouth bass	L	1.13	-	1.15	-	-	-	-	-	-	-	-	-	-	-
Northern pike	L	-	-	-	-	-	-	-	-	-	-	-	0.86	1.2	1.13
Pumpkinseed x redbreas	L	-	-	0.27	-	-	-	-	-	-	-	-	-	-	-
Pumpkinseed	L	-	-	0.03	0.2	0.18	-	-	-	-	-	0.04	-	-	-
Redbreast sunfish	L	1.26	-	0.03	0.37	0.47	-	-	0.09	-	-	0.13	-	-	-
White catfish	L	4.76	6.27	4.33	-	-	-	-	-	-	-	1.26	-	-	-
White perch	L	1.89	1.86	1.53	-	-	-	-	-	-	-	-	-	-	-
Yellow bullhead	L	-	-	-	-	-	-	-	-	-	-	0.18	-	-	-
Yellow perch	L	0.58	-	0.22	0.35	0.32	-	-	0.11	-	-	0.14	-	0.12	0.04
Smallmouth bass	L	1.02	1.33	1.2	0.95	1.41	0.51	0.3	0.84	0.51	0.37	0.53	0.35	0.85	0.48
Bluegill	Z	0.89	-	0.19	0.13	0.25	-	-	-	-	-	0.15	-	-	0.16
Brown bullhead	Z	0.38	-	0.62	-	-	-	-	-	-	-	-	-	-	-
Common carp	Z	3.88	-	12.07	-	-	-	-	-	-	-	-	-	-	-
American eel	Z	-	-	1.04	2.36	5.3	-	-	-	-	-	-	-	-	-
Largemouth bass	Z	0.39	-	1.15	-	-	-	-	-	-	-	-	-	-	-
Northern pike	Z	-	-	-	-	-	-	-	-	-	-	-	1.33	1.49	1.03
Pumpkinseed	Z	-	-	0.11	0.16	0.22	-	-	-	-	-	0.08	-	-	-
Redbreast sunfish	Z	0.09	-	0.15	0.2	0.24	-	-	0.71	-	-	-	-	-	-
White catfish	Z	2.22	2.55	3.4	-	-	-	-	-	-	-	0.59	-	-	-
White perch	Z	0.84	-	1.26	0.87	1.01	-	-	-	-	-	0.51	-	0.49	-
Yellow bullhead	Z	-	-	-	-	-	-	-	-	-	-	0.05	-	-	-
Yellow perch	Z	0.07	-	0.21	0.24	0.26	-	-	-	-	-	0.17	-	0.16	0.11
Smallmouth bass	Z	0.45	-	0.84	0.59	1.13	0.43	0.48	0.87	0.32	0.36	0.28	0.58	0.88	0.98
Bluegill	F	-	-	-	-	-	-	-	-	0.68	-	0.41	-	-	1.30
Brown bullhead	F	-	-	-	-	-	-	-	-	0.95	-	0.32	-	-	-
Northern pike	F	-	-	-	-	-	-	-	-	-	-	10.01	1.06	3.69	6.61
Pumpkinseed	F	-	-	-	-	-	-	-	-	0.21	-	0.27	-	-	-
Smallmouth bass	F	-	-	-	-	-	-	-	-	-	-	1.01	-	-	-
Yellow perch	F	-	-	-	-	-	-	-	-	0.36	-	0.49	-	0.43	0.29
Smallmouth bass	HS	-	-	-	-	-	0.51	-	-	-	-	-	-	-	-
Brown trout	H	-	-	-	-	-	-	-	0.12	0.03	0.1	0.09	-	0.01	0.01

APPENDIX F

Summary of ANCOVA Models Used in Statistical Analyses of the Text, Showing All Statistically Significant Terms Retained

Model terms for TPCB smallmouth bass (all years except 1986, all stations)

Response variable:	ln(TPCB)
Main effects:	year, station, sex
Covariates:	ln(river age), ln(% lipid)
Interactions:	year × station, station × sex, sex × ln(%lipid), station × ln(river age), station × ln(% lipid), year × ln(% lipid)
Model r^2:	0.73

Model terms for CTPCB smallmouth bass (1992–2010, all stations)

Response variable:	ln(CTPCB)
Main effects:	year, station, sex
Covariates:	ln(river age), ln(% lipid)
Interactions:	year × station, station × ln(% lipid), station × ln(river age), year × ln(%lipid)
Model r^2:	0.72

Model terms for TPCB smallmouth bass at West Cornwall (all years)

Response variable:	ln(TPCB)
Main effects:	year, sex
Covariates:	ln(% lipid), ln(river age)
Interactions:	year × ln(river age)
Model r^2:	0.73

Model terms for TPCB smallmouth bass at Bulls Bridge (all years)

Response variable:	ln(TPCB)
Main effects:	year
Covariates:	ln(% lipid), ln(river age)
Interactions:	year × ln(% lipid), sex × ln(river age)
Model r^2:	0.72

Model terms for TPCB smallmouth bass at Lake Lillinonah (all years)

Response variable:	ln(TPCB)
Main effects:	year
Covariates:	ln(river age)
Interactions:	year × ln(% lipid), year x ln(river age)
Model r^2:	0.76

Model terms for TPCB smallmouth bass at Lake Zoar (all years except 1986)

Response variable:	ln(TPCB)
Main effects:	year
Covariates:	ln(% lipid), ln(river age)
Interactions:	(none)
Model r^2:	0.50

Model terms for TPCB brown trout at West Cornwall (all years)

Response variable:	ln(TPCB)
Main effects:	year
Covariates:	ln(%lipid), ln(river age)
Interactions:	year × ln(river age), year × ln(% lipid), ln(%lipid) × ln(river age)
Model r^2:	0.75

Model terms for CTPCB brown trout at West Cornwall (1992–2010)

Response variable:	ln(CTPCB)
Main effects:	year
Covariates:	ln(% lipid), ln(river age)
Interactions:	year × ln(river age), year × ln(% lipid), ln(river age) x ln(% lipid)
Model r^2:	0.72

Model terms for CTPCB smallmouth bass at West Cornwall (1992–2010)

Response variable:	ln(CTPCB)
Main effects:	year, sex
Covariates:	ln(% lipid)
Interactions:	(none)
Model r^2:	0.50

Model terms for CTPCB smallmouth bass at Bulls Bridge (1992–2010)

Response variable:	ln(CTPCB)
Main effects:	year, sex
Covariates:	ln(% lipid)
Interactions:	year × ln(% lipid), sex × ln(river age)
Model r^2:	0.63

Model terms for CTPCB smallmouth bass at Lake Lillinonah (1992–2010)

Response variable:	ln(CTPCB)
Main effects:	year
Covariates:	ln(river age)
Interactions:	year × ln(% lipid)
Model r^2:	0.70

Model terms for CTPCB smallmouth bass at Lake Zoar (1992–2010)

Response variable:	ln(CTPCB)
Main effects:	year
Covariates:	ln(river age)
Interactions:	(none)
Model r^2:	0.49

APPENDIX G

Summary of Total PCB Concentrations (mg/kg wet weight) of Fillets of Brown Trout Collected in Academy Surveys of the Housatonic River.

Year	Hatchery	West Cornwall – Age Class (years)						
		< 0.20	0.20–0.33	0.34–0.99	1.00–1.99	2.00–2.99	3.00–3.99	> 3.99
Geometric Mean of CTPCB								
2010	0.01	-	0.83	1.62	1.92	3.33	-	3.03
2008	0.01	-	-	-	1.93	1.04	-	3.36
2006	0.01	-	1.15	1.01	3.86	-	-	-
2004	0.09	-	1.42	1.83	2.95	-	-	-
2002	0.1	-	1.13	1.33	1.92	1.08	3.38	3.06
2000	0.03	1.39	1.28	-	2.72	2.35	3.46	–
1998	0.12	-	1.27	1.68	3.31	4.09	11.13	–
1996	0.04	0.12	1.54	1.84	2.82	-	4.77	6.89
1994	0.04	-	1.07	0.81	-	3.88	-	-
1992	-	3.32	6.88	6.73	10.77	9.65	-	-
Geometric Mean of TPCB								
2010	0.01	-	0.97	1.86	2.22	3.92	-	3.80
2008	0.01	-	-	-	2.30	1.94	-	4.09
2006	0.01	-	1.65	1.19	2.87	-	-	-
2004	0.09	-	1.63	2.01	4.25	-	-	-
2002	0.10	-	1.10	1.29	1.86	1.04	3.32	3.00
2000	0.04	1.38	1.29	-	2.73	3.31	3.10	-
1998	0.12	-	1.28	1.64	3.22	4.18	11.16	-
1996	0.03	0.11	1.65	2.00	3.13	-	5.15	7.93
1994	0.04	-	1.18	0.84	-	5.01	-	-
1992	-	4.18	8.72	8.69	14.03	12.54	-	-
1990	-	-	-	4.93	6.84	7.83	6.23	-
1989	0.03	-	-	-	-	-	-	-
1988	0.06	-	3.75	4.42	7.06	5.22	10.40	5.74
1987	0.03	-	-	-	-	-	-	-
1986	-	-	3.30	-	5.16	7.34	8.55	16.17
1984	-	-	1.37	-	6.89	4.97	7.56	-
Percent Lipid								
2010	14.22	-	2.98	4.43	4.35	5.81	-	2.29
2008	8.87	-	-	-	2.99	3.26	-	3.61
2006		-	4.19	3.50	3.42	-	-	-
2004	8.89	-	4.76	4.00	4.67	-	-	-
2002	7.85	-	3.51	2.74	5.32	4.67	4.07	4.88
2000	5.69	4.00	2.57	-	4.84	3.42	5.51	-
1998	2.47	-	2.04	1.87	3.88	1.21	5.29	-
1996	3.54	2.25	1.78	1.00	2.15	-	1.08	1.03
1994	5.87	-	2.74	1.79	-	2.33	-	-
1992	-	3.99	3.99	2.69	6.29	4.60	-	-
1990	-	-	-	1.19	1.83	0.56	1.68	-
1989	3.60	-	-	-	-	-	-	-
1988	1.82	-	1.88	1.32	4.32	4.37	4.64	3.60
1987	0.40	-	-	-	-	-	-	-
1986	-	-	4.04	-	3.83	3.67	3.70	4.35
1984	-	-	2.81	-	3.30	2.85	3.35	-

APPENDIX H

Geometric Mean PCB Concentration in Benthic Insects from the Housatonic River (1992-2010)

Table H-1. Geometric mean total PCB concentrations (mg/kg wet weight) in benthic insects from the Housatonic River, 1992–2010. Both Aroclor-based and congener-based estimates of total PCBs are shown (TPCB and CTPCB, respectively). Caddisflies are filter feeders, while dobsonflies and stoneflies are predators.

Year	PCB Measure	Caddisflies (Hydropsychidae)	Dobsonflies (Corydalidae)	Stoneflies (Perlidae)
1992	TPCB	3.94	7.45	3.71
	CTPCB	3.01	5.48	3.01
1994	TPCB	1.92	2.93	1.09
	CTPCB	1.8	2.49	1.01
1996	TPCB	2.69	3.13	2.43
	CTPCB	2.5	2.65	2.29
1998	TPCB	1.05	3.94	0.54
	CTPCB	0.86	2.92	0.4
2001	TPCB	0.9	1.81	0.53
	CTPCB	0.97	1.83	0.57
2002	TPCB	0.58	0.94	0.46
	CTPCB	0.63	0.99	0.51
2005	TPCB	0.6	0.55	0.54
	CTPCB	0.51	0.44	0.5
2006	TPCB	1.61	1.93	0.66
	CTPCB	1.33	1.46	0.64
2008	TPCB	0.94	1.76	0.88
	CTPCB	0.78	1.45	0.75
2010	TPCB	0.8	2.04	0.67
	CTPCB	0.67	1.63	0.61

APPENDIX I

40 CFR 136, Appendix B: Protocol for Detection Limit Calculations. Revision 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, *i.e.*, a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} X_i\right)^2}{n}\right] \quad S = \left(S^2\right)^{\frac{1}{2}}$$

where:

Xι; i=l to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=l to n.

6. (a) Compute the MDL as follows:

MDL = t(n-1,1-α=0.99) (S)

where:

MDL = the method detection limit

t(n-1,1-α=.99)= the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2 /df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute The final MDL according to the following equation:

$$MDL=2.681\ (S_{pooled})$$

where 2.681 is equal to $t(12,1-\alpha=.99)$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL

UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

Tables of Students' t Values at the 99 Percent Confidence Level

Number of replicates	Degrees of freedom (n-1)	$t_{cn-1,.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

APPENDIX J

2010 Detection Limit Calculations

Matrix blanks were generated to monitor possible laboratory contamination and to calculate the detection limits for PCBs. Each matrix blank, consisting of approximately 30 g of clean Na_2SO_4, was analyzed using the same procedures as the samples.

The detection limit was estimated as the blank area plus three times the standard deviation of the average blank peak areas. The method detection is reported on a mass per mass basis (dividing by an average extraction mass of 5.05 ng; Table J-1). The matrix blank-based detection limits for PCBs ranged from 0.004 ng/g (congener 85) to 8.15 ng/g (congener 3). Based on the matrix blanks, the average detection limit for individual PCBs was 0.27 ng/g and that for total PCBs was 22 ng/g.

Table J-1. The concentrations of all congeners in all blank samples and the calculations used to obtain the Minimum Detection Limit for congeners in the 2010 ANS Housatonic River survey.

Blank ID	**Concentration (ng/g)**										**Average Concentration**	**Standard Deviation**	**Avg + (3*StDev)**	**Minimum Detection Limit***
	020711A	**020711B**	**20911**	**21411**	**21611**	**22111**	**22311**	**22511**	**22811**	**30211**				
1	14.90	10.23	7.73	7.51	7.86	8.42	9.11	8.01	8.46	9.72	9.20	2.19	15.8	**3.12**
3	36.99	25.54	32.12	23.08	21.04	24.58	22.73	25.28	29.08	26.48	26.69	4.83	41.2	**8.15**
4+10	3.52	3.67	4.35	3.82	3.61	2.88	3.02	2.56	2.40	3.10	3.30	0.61	5.1	**1.01**
7	0.44	0.85	0.76	0.64	0.25	0.22	0.29	0.23	0.37	0.36	0.44	0.23	1.1	**0.22**
6	0.82	0.64	0.82	0.58	0.65	0.61	0.55	0.56	0.72	0.63	0.66	0.10	1.0	**0.19**
8+5	2.58	2.03	2.29	2.21	1.61	1.47	1.51	2.08	1.74		1.95	0.39	3.1	**0.61**
19	0.58	0.39	0.42	0.42	0.38	0.37	0.41	0.40	0.67	0.56	0.46	0.10	0.8	**0.15**
12+13	0.58	0.58	0.68	0.59	0.72	0.64	0.56	0.62	0.77	0.63	0.64	0.07	0.8	**0.17**
18	0.53	0.53		0.58	0.53	0.60	0.59	0.62	0.56	0.64	0.57	0.04	0.7	**0.14**
17	0.58	0.54	0.57	0.57	0.47	0.47	0.53	0.57	0.55	0.56	0.54	0.04	0.7	**0.13**
24+27	0.23	0.25	0.23	0.18	0.37	0.23	0.18	0.22		0.29	0.24	0.06	0.4	**0.08**
16+32	0.55	0.61	0.56	0.65	0.84	0.66	0.52	0.65	0.63	0.59	0.63	0.09	0.9	**0.18**
29	0.19	0.34	0.33	0.29	0.32	0.18	0.15	0.26	0.18	0.15	0.24	0.08	0.5	**0.09**
26	0.53	0.44	0.41	0.43	0.45	0.45	0.37	0.43	0.42	0.46	0.44	0.04	0.6	**0.11**
25	0.29	0.35	0.32	0.29	0.31	0.31	0.27	0.34	0.32	0.33	0.31	0.02	0.4	**0.08**
31+28	0.48	0.47	0.58	0.52	0.56	0.57	0.50	0.61	0.57	0.54	0.54	0.05	0.7	**0.13**
33+21	0.43	0.51	0.46	0.45	0.67	0.49	0.42	0.51	0.42	0.48	0.48	0.07	0.7	**0.14**
53	0.08	0.10	0.09	0.09	0.13	0.09	0.08	0.10	0.08	0.09	0.09	0.01	0.1	**0.03**
22	0.52	0.64	0.55	0.51	1.20	0.74	0.69	0.59	0.62	0.56	0.66	0.20	1.3	**0.25**
45	0.37	0.44	0.40	0.35	0.41	0.40	0.43	0.43	0.35	0.38	0.40	0.03	0.5	**0.10**
46	0.41	0.46	0.42	0.40	0.58	0.45	0.52	0.48	0.43	0.47	0.46	0.05	0.6	**0.12**
52	0.44	0.42	0.40	0.38	0.41	0.40	0.48	0.49	0.49	0.47	0.44	0.04	0.6	**0.11**
49	0.40	0.39	0.39	0.45	0.51	0.45	0.36	0.50	0.38	0.45	0.43	0.05	0.6	**0.12**
47	0.65	0.73	0.87	0.48	0.43	0.45	0.48	0.60	0.45	0.43	0.56	0.15	1.0	**0.20**
48	0.60	0.34	0.50	0.37	0.36	0.38	0.42	0.67	0.55	0.43	0.46	0.11	0.8	**0.16**
44	0.33	0.33	0.38	0.41	0.37	0.41	0.44	0.42	0.40	0.38	0.39	0.03	0.5	**0.10**
37	0.76	0.73	0.77	0.72	0.91	0.80	0.90	1.00	0.88	0.92	0.84	0.10	1.1	**0.22**
42	0.27	0.23	0.29	0.31	0.25	0.23	0.29	0.26	0.26	0.23	0.26	0.03	0.3	**0.07**
41+71	0.46	0.47	0.43	0.45	0.41	0.42	0.41	0.41	0.36	0.47	0.43	0.03	0.5	**0.10**
40	0.33	0.50	0.98	0.39	0.36	0.37	0.46	0.51	0.35	0.35	0.46	0.19	1.0	**0.21**
100	0.12	0.13	0.13	0.12	0.14	0.13	0.13	0.17	0.13	0.13	0.13	0.01	0.2	**0.04**
63	0.32	0.37	0.31	0.28	0.29	0.35	0.27	0.40	0.33	0.32	0.32	0.04	0.4	**0.09**
74	0.37	0.34	0.47	0.30	0.33	0.33	0.33	0.38	0.32	0.38	0.36	0.05	0.5	**0.10**
70+76	0.47	0.48	0.56	0.49	0.48		0.41	0.57	0.48	0.47	0.49	0.05	0.6	**0.13**
66	0.53	0.46	0.57	0.51	0.51	0.52	0.51	0.50	0.49	0.51	0.51	0.03	0.6	**0.12**
95	0.37	0.34	0.37	0.41	0.40	0.45	0.32	0.41	0.44	0.43	0.39	0.04	0.5	**0.10**
91	0.31	0.50	0.67	0.82	0.40	0.34	0.45	0.74	0.37	0.33	0.49	0.19	1.0	**0.21**
56+60	0.76	0.80	1.27	0.76	0.79	0.80	0.67	1.13	0.74	0.89	0.86	0.19	1.4	**0.28**
84	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
101	0.24	0.22	0.23	0.25	0.34	0.23	0.27	0.23	0.24	0.26	0.25	0.03	0.4	**0.07**
99	0.23	0.21	0.20	0.20	0.23	0.22	0.25	0.27	0.24	0.23	0.23	0.02	0.3	**0.06**

Table J-1 Continued. The concentrations of all congeners in all blank samples and the calculations used to obtain the Minimum Detection Limit for congeners in the 2010 ANS Housatonic River survey.

Blank ID	**Concentration (ng/g)**										**Average**	**Standard**	**Avg +**	**Minimum**
	020711A	**020711B**	**20911**	**21411**	**21611**	**22111**	**22311**	**22511**	**22811**	**30211**	**Concentration**	**Deviation**	**(3*StDev)**	**Detection**
83	0.18	0.44	0.22	0.17	0.73	0.18	0.18	0.23	0.19	1.54	0.41	0.44	1.7	**0.34**
97	0.26	0.39	0.40	0.31	0.28	0.28	0.25	0.56	0.20	0.21	0.32	0.11	0.6	**0.13**
87	0.17	0.36	0.51	0.29	0.42	0.32	0.13	0.55	0.39	0.16	0.33	0.14	0.8	**0.15**
85	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.00	0.0	**0.00**
136	0.24	0.22	0.25	0.23	0.22		0.22	0.24	0.22	0.23	0.23	0.01	0.3	**0.05**
77+110	0.24	0.29	0.24	0.24	0.29	0.23	0.24	0.27	0.28	0.25	0.26	0.02	0.3	**0.06**
82	0.18	0.22	0.16	0.16	0.18	0.16	0.15	0.20	0.18	0.19	0.18	0.02	0.2	**0.05**
151	0.25	0.24	0.31	0.22	0.25	0.31	0.24	0.27	0.26	0.26	0.26	0.03	0.3	**0.07**
135+144	0.19	0.24	0.20	0.24	0.21	0.22	0.18	0.22	0.22	0.21	0.21	0.02	0.3	**0.05**
107	0.11	0.12	0.10	0.10	0.10	0.11	0.10	0.20	0.11	0.13	0.12	0.03	0.2	**0.04**
149	0.29	0.28	0.28	0.28	0.27	0.28	0.34	0.35	0.28	0.33	0.30	0.03	0.4	**0.08**
118	0.19	0.18	0.27	0.18	0.20	0.21	0.21	0.20	0.26	0.21	0.21	0.03	0.3	**0.06**
131	0.08	0.09	0.07	0.08	0.08	0.08	0.08	0.09	0.08	0.08	0.08	0.00	0.1	**0.02**
146	0.34	0.36	0.35	0.28	0.32	0.31	0.34	0.36	0.35	0.34	0.34	0.02	0.4	**0.08**
153+132+105	0.49	1.52	1.30	1.44	1.39	1.91	0.83	3.16	2.59	1.75	1.64	0.78	4.0	**0.79**
141	0.24	0.28	0.29	0.27	0.27	0.23	0.28	0.28	0.28	0.26	0.27	0.02	0.3	**0.06**
137+176	0.23	0.27	0.25	0.23	0.21	0.26	0.21	0.21	0.27	0.20	0.23	0.03	0.3	**0.06**
163+138	0.28	0.26	0.28	0.24	0.25	0.27	0.27	0.34	0.25	0.26	0.27	0.03	0.4	**0.07**
158	0.32	1.40	1.35	1.02	0.68	1.17	0.78	1.65	1.39	1.07	1.08	0.40	2.3	**0.45**
129	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.00	0.0	**0.01**
187+182	0.46	0.43	0.48	0.44	0.43	0.48	0.46	0.50	0.46	0.62	0.48	0.05	0.6	**0.13**
183	0.33	0.31	0.28	0.27	0.29	0.34	0.28	0.36	0.29	0.31	0.31	0.03	0.4	**0.08**
128	0.18	0.17	0.18	0.16	0.17	0.17	0.16	0.17	0.20	0.21	0.18	0.02	0.2	**0.05**
185	0.16	0.19	0.18	0.16	0.16	0.16	0.20	0.19	0.18	0.21	0.18	0.02	0.2	**0.05**
174	0.26	0.20	0.25	0.23	0.21	0.20	0.20	0.24	0.20	0.24	0.22	0.02	0.3	**0.06**
177	0.22	0.22	0.22	0.23	0.21	0.25	0.21	0.28	0.24	0.23	0.23	0.02	0.3	**0.06**
202+171	0.18	0.17	0.21	0.17	0.18	0.20	0.18	0.23	0.24	0.24	0.20	0.03	0.3	**0.06**
157+200	0.40	0.34	0.34	0.33	0.34	0.32	0.29	0.43	0.33	0.37	0.35	0.04	0.5	**0.09**
172+197	0.25	0.26	0.36	0.27	0.25	0.24	0.22	0.30	0.30	0.24	0.27	0.04	0.4	**0.08**
180	0.18	0.51	0.27	0.20	0.26	0.24	0.21	0.22	0.19	0.18	0.25	0.10	0.5	**0.11**
193	0.34	0.33	0.33	0.41	0.35	0.32	0.31	0.41	0.32	0.31	0.34	0.04	0.5	**0.09**
191	0.25	0.25	0.28	0.30	0.24	0.24	0.22	0.26	0.25	0.25	0.25	0.02	0.3	**0.06**
199	0.12	0.12	0.14	0.11	0.11	0.13	0.18	0.18	0.11	0.12	0.13	0.03	0.2	**0.04**
170+190	0.25	0.30	0.26	0.35	0.28	0.26	0.29	0.29	0.30	0.26	0.28	0.03	0.4	**0.07**
201	0.25	0.27	0.28	0.25	0.30	0.27	0.25	0.36	0.27	0.26	0.28	0.03	0.4	**0.07**
203+196	0.26	0.26	0.30	0.27	0.29	0.24	0.29	0.26	0.26	0.29	0.27	0.02	0.3	**0.07**
208+195	0.35	0.40	0.38	0.30	0.32	0.36	0.32	0.38	0.30	0.35	0.35	0.03	0.5	**0.09**
207	0.16	0.21	0.18	0.16	0.15	0.16	0.20	0.18	0.17	0.17	0.17	0.02	0.2	**0.05**
194	0.13	0.12	0.11	0.12	0.12	0.12	0.12	0.17	0.13	0.12	0.13	0.02	0.2	**0.03**
205	0.14	0.13	0.14	0.12	0.14	0.13	0.19	0.14	0.14	0.14	0.14	0.02	0.2	**0.04**
206	0.20	0.22	0.18	0.23	0.20	0.19	0.30	0.20	0.27	0.21	0.22	0.04	0.3	**0.07**
209	0.11	0.22	0.30	0.26	0.16	0.29	0.13	0.23	0.13	0.12	0.20	0.07	0.4	**0.08**
Total (ng)	83	70	76	64	62	64	62	71	70	68	69	14	110	22

* Minimum Detection Limit was obtained by dividing the previous column by an average extration mass of 5.05ng

APPENDIX K

Summary of Supplemental Fish Sampling Effort

In the 2010 study, fish samples in addition to those required for the biennial monitoring program were collected at the request of CTDEP. These supplemental samples were collected from Falls Village, Bulls Bridge, Lake Lillinonah, and Lake Zoar. A total of 12 northern pike, 40 yellow perch, and 20 bluegill were collected. Northern pike were collected at each of the following stations: Falls Village (on 9 August 2010), Bulls Bridge (on 10 August 2010), and Lakes Lillinonah and Zoar (both on 11 August 2010). Yellow perch were collected at Falls Village (on 9 August 2010), Bulls Bridge (on 10 August 2010), Lake Lillinonah (on 11 August 2010), and Lake Zoar (on 11 and 12 August 2010). Bluegills were collected at Falls Village (on 9 August 2010), Bulls Bridge (on 10 August 2010), and Lakes Lillinonah and Zoar (both on 11 and 12 August 2010).

Collections of supplemental fish samples at all four stations were done at the same time and with the same techniques as collections of the primary species, as detailed in the methods section of the report and Table 1. Methods of specimen handling, sample preparation, and sample analyses were identical to those for the primary specimens, except that yellow perch and bluegill were composited prior to extraction and analysis. The yellow perch and bluegill samples were combined into 5-fish composites, with each composite consisting of specimens of similar size. Northern pike were analyzed as single individuals because of their lower abundance.

Results from the 2010 supplemental sampling effort are summarized in Tables K-1 and K-2. TPCB ranges (minimum to maximum) were 0.56–14.41 mg/kg (wet weight) for northern pike, 0.04–0.48 mg/kg for yellow perch, and 0.16-1.56 mg/kg for bluegill. CTPCB ranges were 0.48–11.57 mg/kg for northern pike, 0.04–0.39 mg/kg for yellow perch, and 0.13-1.30 mg/kg for bluegill. Thus, all northern pike specimens had greater TPCB and CTPCB concentrations than any bluegill or yellow perch specimens. This finding is consistent with results of previous supplemental fish sampling, where larger piscivorous species such as northern pike and white catfish tended to show higher PCB concentrations than did smaller species such as bluegill, white perch, and yellow perch. There also appeared to be a tendency for TPCB and CTPCB concentrations to decrease in the downstream direction.

Of the 24 supplemental samples analyzed (some as individual fish and some as composites), 3 had TPCB and CTPCB concentrations greater than the FDA fish consumption limit of 2.0 mg/kg wet weight and 3 others had TPCB (but not CTPCB) concentrations above that limit. All six of these were individual northern pike specimens (three from Falls Village (both TPCB and CTPCB), two from Bulls Bridge and one from Lake Zoar (TPCB only)). These fish represent 50% of the northern pike collected and ranged in size from 72.2 to 105.2 cm. The pike with the highest concentrations came from Falls Village, followed by the two from Bulls Bridge, and the pike from Lake Zoar which had the lowest concentration of the six fish despite being the largest collected.

Table K-1. Summary of total PCB concentrations and ancillary data in fishes from supplemental samples in 2010. For composite samples (yellow perch, bluegill), sex, length, and total weight are listed for each fish in the sample; lipid percentage and TPCB and CTPCB concentrations for the composite are then listed on a separate line. "Month" denotes the collection month. Station codes: FV = Falls Village, BB = Bulls Bridge, LL = Lake Lillinonah, LZ = Lake Zoar.

Species	Number of samples		Station	Month collected	Sex	Total Length (cm)		Total Weight (g)	Lipid	TPCB	CTPCB
	Samples	Individuals				Field	Lab	Lab	%	mg/kg	mg/kg
Northern pike	1	1	FV	August	M	72.6	72.2	2414.97	0.66	2.45	2.01
Northern pike	1	1	FV	August	M	81.8	81.1	3783.40	2.15	14.41	11.57
Northern pike	1	1	FV	August	M	91.1	90.5	5190.00	2.48	7.58	6.23
Northern pike	1	1	BB	August	M	91.3	90.9	5380.00	4.31	2.30	1.89
Northern pike	1	1	BB	August	M	72.9	72.2	2397.00	0.45	0.72	0.60
Northern pike	1	1	BB	August	M	75.9	75.9	3030.23	1.12	2.36	1.95
Northern pike	1	1	LL	August	M	70.9	71.2	2322.22	1.06	1.25	1.07
Northern pike	1	1	LL	August	F	79.5	79.5	2907.51	1.28	0.97	0.82
Northern pike	1	1	LL	August	F	88.6	87.5	4131.12	2.81	1.79	1.50
Northern pike	1	1	Z	August	M	88.0	87.3	4750.00	0.61	0.56	0.48
Northern pike	1	1	Z	August	F	85.8	84.5	4135.09	3.18	1.17	0.98
Northern pike	1	1	Z	August	F	106.0	105.2	8100.00	2.39	2.03	1.64
Yellow perch	2	10	FV	August	F	23.5	23.3	172.63	-	-	-
Yellow perch	-	-	FV	August	F	23.0	23.0	158.40	-	-	-
Yellow perch	-	-	FV	August	M	23.2	22.9	171.18	-	-	-
Yellow perch	-	-	FV	August	F	25.5	25.3	205.28	-	-	-
Yellow perch	-	-	FV	August	M	24.4	24.3	182.00	-	-	-
						composite sample (5 fish):			1.03	0.35	0.29
Yellow perch	-	-	FV	August	F	18.6	18.2	70.90	-	-	-
Yellow perch	-	-	FV	August	M	17.9	17.6	70.49	-	-	-
Yellow perch	-	-	FV	August	F	17.5	17.2	61.11	-	-	-
Yellow perch	-	-	FV	August	F	17.3	17.3	63.27	-	-	-
Yellow perch	-	-	FV	August	F	17.4	17.5	63.54	-	-	-
						composite sample (5 fish):			0.79	0.10	0.08
Yellow perch	2	10	BB	August	F	30.9	31.0	408.75	-	-	-
Yellow perch	-	-	BB	August	F	31.4	31.4	408.19	-	-	-
Yellow perch	-	-	BB	August	F	32.6	32.1	390.71	-	-	-
Yellow perch	-	-	BB	August	F	30.4	30.5	413.49	-	-	-
Yellow perch	-	-	BB	August	M	30.7	30.5	374.97	-	-	-
						composite sample (5 fish):			0.92	0.48	0.39
Yellow perch	-	-	BB	August	M	18.3	18.0	69.77	-	-	-
Yellow perch	-	-	BB	August	F	18.2	18.1	68.69	-	-	-
Yellow perch	-	-	BB	August	F	18.7	18.5	73.35	-	-	-
Yellow perch	-	-	BB	August	M	19.2	19.1	80.43	-	-	-
Yellow perch	-	-	BB	August	M	18.0	17.7	64.90	-	-	-
						composite sample (5 fish):			0.87	0.20	0.17
Yellow perch	2	10	LL	August	M	24.6	24.6	173.83	-	-	-
Yellow perch	-	-	LL	August	F	23.9	23.8	190.76	-	-	-
Yellow perch	-	-	LL	August	F	24.9	24.7	181.34	-	-	-
Yellow perch	-	-	LL	August	M	24.9	24.7	190.77	-	-	-
Yellow perch	-	-	LL	August	F	23.8	23.4	139.63	-	-	-
						composite sample (5 fish):			1.00	0.04	0.04
Yellow perch	-	-	LL	August	M	17.0	16.9	52.15	-	-	-
Yellow perch	-	-	LL	August	F	17.9	17.9	57.40	-	-	-
Yellow perch	-	-	LL	August	F	17.9	17.9	56.19	-	-	-
Yellow perch	-	-	LL	August	F	17.6	17.6	58.22	-	-	-
Yellow perch	-	-	LL	August	F	18.2	18.2	65.01	-	-	-
						composite sample (5 fish):			0.45	0.05	0.04
Yellow perch	2	10	Z	August	F	21.8	21.7	111.92	-	-	-
Yellow perch	-	-	Z	August	F	26.1	25.9	194.67	-	-	-
Yellow perch	-	-	Z	August	F	22.6	22.4	111.93	-	-	-
Yellow perch	-	-	Z	August	F	22.1	22.0	117.23	-	-	-
Yellow perch	-	-	Z	August	F	18.6	18.5	72.44	-	-	-
						composite sample (5 fish):			0.69	0.13	0.11

Table K-1 continued. Summary of total PCB concentrations and ancillary data in fishes from supplemental samples in 2010. For composite samples (yellow perch, bluegill), sex, length, and total weight are listed for each fish in the sample; lipid percentage and TPCB and CTPCB concentrations for the composite are then listed on a separate line. "Month" denotes the collection month. Station codes: FV = Falls Village, BB = Bulls Bridge, LL = Lake Lillinonah, LZ = Lake Zoar.

Species	Number of samples		Station	Month collected	Sex	Total Length (cm)		Total Weight (g)	Lipid	TPCB	CTPCB
	Samples	Individuals				Field	Lab	Lab	%	mg/kg	mg/kg
Yellow perch	-	-	Z	August	F	18.3	18.2	66.32	-	-	-
Yellow perch	-	-	Z	August	M	18.5	18.4	69.45	-	-	-
Yellow perch	-	-	Z	August	M	18.3	18.1	61.97	-	-	-
Yellow perch	-	-	Z	August	F	18.0	17.9	63.68	-	-	-
Yellow perch	-	-	Z	August	F	24.0	24.0	145.25	-	-	-
						composite sample (5 fish):			0.75	0.13	0.12
Blue gill	1	5	FV	August	M	20.8	20.5	225.42	-	-	-
Blue gill	-	-	FV	August	M	19.8	19.5	198.29	-	-	-
Blue gill	-	-	FV	August	M	19.0	19.0	173.83	-	-	-
Blue gill	-	-	FV	August	M	20.6	20.6	243.56	-	-	-
Blue gill	-	-	FV	August	M	21.8	21.7	261.22	-	-	-
						composite sample (5 fish):			3.07	1.56	1.30
Blue gill	1	5	BB	August	M	19.4	19.4	175.82	-	-	-
Blue gill	-	-	BB	August	M	19.8	19.9	202.21	-	-	-
Blue gill	-	-	BB	August	F	22.0	21.8	237.84	-	-	-
Blue gill	-	-	BB	August	M	19.5	19.2	184.88	-	-	-
Blue gill	-	-	BB	August	F	20.2	20.1	212.46	-	-	-
						composite sample (5 fish):			1.75	0.55	0.48
Blue gill	1	5	LL	August	F	20.3	20.1	155.63	-	-	-
Blue gill	-	-	LL	August	M	19.5	19.5	141.65	-	-	-
Blue gill	-	-	LL	August	F	20.2	20.2	148.63	-	-	-
Blue gill	-	-	LL	August	M	18.9	18.9	142.98	-	-	-
Blue gill	-	-	LL	August	M	19.4	19.3	135.42	-	-	-
						composite sample (5 fish):			0.70	0.16	0.13
Blue gill	1	5	Z	August	F	20.6	20.5	185.38	-	-	-
Blue gill	-	-	Z	August	M	19.9	19.5	137.52	-	-	-
Blue gill	-	-	Z	August	M	19.1	18.9	153.72	-	-	-
Blue gill	-	-	Z	August	M	18.8	18.6	148.47	-	-	-
Blue gill	-	-	Z	August	F	19.9	19.7	147.67	-	-	-
						composite sample (5 fish):			0.79	0.18	0.16

Table K-2. Summary of PCB concentrations in fishes from supplemental analyses in 2010. Concentrations are means of values from composite (bluegill and perch) or individual samples (pike). % lipid value is the arithmetic mean if there was more than one sample.

Species	Station	Month	Number of samples		Total Length (cm)			% Lipid	Minimum		Maximum		Arithmetic mean		Geometric Mean	
			Samples	Ind.	Ave	Min	Max		CTPCB	TPCB	CTPCB	TPCB	CTPCB	TPCB	CTPCB	TPCB
Bluegill																
	FV	August	1	5	20.3	19.0	21.7	3.07	-	-	-	-	1.30	1.56	1.30	1.56
	BB	August	1	5	20.1	19.2	21.8	1.75	-	-	-	-	0.48	0.55	0.48	0.55
	LL	August	1	5	19.6	18.9	20.2	0.70	-	-	-	-	0.13	0.16	0.13	0.16
	Z	August	1	5	19.4	18.6	20.5	0.79	-	-	-	-	0.16	0.18	0.16	0.18
Yellow Perch																
	FV	August	2	10	20.7	17.2	25.3	0.91	0.08	0.10	0.29	0.35	0.18	0.22	0.15	0.18
	BB	August	2	10	24.7	17.7	32.1	0.89	0.17	0.20	0.39	0.48	0.28	0.34	0.26	0.31
	LL	August	2	10	21.0	16.9	24.7	0.73	0.04	0.04	0.04	0.05	0.04	0.05	0.04	0.05
	Z	August	2	10	20.7	17.9	25.9	0.72	0.11	0.13	0.12	0.13	0.11	0.13	0.11	0.13
Northern pike																
	FV	August	3	3	81.3	72.2	90.5	1.76	2.01	2.45	11.57	14.41	6.61	8.15	5.25	6.45
	BB	August	3	3	79.7	72.2	90.9	1.96	0.60	0.72	1.95	2.36	1.48	1.79	1.31	1.57
	LL	August	3	3	79.4	71.2	87.5	1.72	0.82	0.97	1.50	1.79	1.13	1.34	1.09	1.30
	Z	August	3	3	92.3	84.5	105.2	2.06	0.48	0.56	1.64	2.03	1.03	1.26	0.92	1.10

APPENDIX L

Linear Contrasts of TPCB and CTPCB Concentrations Among Groups of Years

Introduction and Methods

Throughout the many years of these surveys since 1984, including the most recent year, statistical comparisons among different years have been based on pairwise comparisons of least squares means concentrations, i.e., a separate test has been done for each pair of years. This was an appropriate procedure, especially in earlier years when the temporal pattern of concentrations was unclear and no *a priori* hypotheses could be defined. Furthermore, the exact statistical models for adjusting concentrations for differences in sex, lipid and fish age changed with each additional year's data, since the additional data provided greater resolution of these covariate effects. However, this approach is less appropriate at this point in the monitoring program, since the patterns of earlier years have been established. Because of the amount of earlier data, covariate models do not change greatly with the addition of each additional year's data. There is a major drawback to use of pairwise comparisons, since statistical power is lost with increasing numbers of years of data. Statistical power is the ability to reject a null hypothesis when that hypothesis is false. For example, statistical power often decreases with decreasing sample size, smaller deviation of the true value from that posited by the null hypothesis, and higher replicate variation among samples. For a given data set, statistical power is related to the probability of rejecting the null hypothesis when it is true (false positives). For example, using a less stringent p-value to determine statistical significance increases statistical power (it's easier to find a significant difference), but also increases the probability of finding significance when there is no real effect. Thus, test procedures balance the desire for greater statistical power and lower probability of false positives. In the case of pairwise comparisons, statistical power is lost by the need to adjust the level of significance to reduce the frequency of false positives.

Pairwise comparisons involve a large number of separate tests, n*(n-1) tests for n years of data. As a result, there is a high probability of finding some proportion of tests to be significant even if there is no real difference. For example, with an alpha level of 0.05, one significant result would be expected for every 20 tests done, if tests were independent. Pairwise-comparison tests, including the HSD test used for the Housatonic PCB data, are designed to control for this potential error. One result of this correction is that the statistical power of comparisons decreases with the number of tests done – i.e., as the number of tests increases, the difference between pair members has to be greater to be demonstrated as significantly different. For the Housatonic PCB data, there are data for 14 different years for TPCB and 10 different years for CTPCB, so the loss of power may be substantial.

An alternate approach to testing the significance of temporal trends is based on defining and testing a much smaller number of statistical hypotheses involving the comparison of the recent years' data with data from selected groups of previous years. This alternate approach provides greater statistical power, since it focuses on a limited number of statistical questions. Moreover, it limits those questions to the relationship between the most recent years of data and certain groups of prior years, rather than making comparisons among individual years within earlier groups of years, which are no longer of primary interest in assessing long-term trends in PCB concentrations.

The alternate approach uses the statistical method of linear contrasts. Tests are performed on linear combinations of yearly data (for example, the average of a group of years is a linear combination, with each year given equal weight). As with the earlier method, tests are performed on least squares means.

For the Housatonic PCB data, previous studies showed a pattern of moderate concentrations from 1984-1986, higher concentrations in 1998-1992, and lower concentrations from 1994 to the present. Based on this pattern, the linear contrasts approach has been used to compare the average of the three most recent years (in this case, the 2006, 2008, and 2010 surveys) – which was used in lieu of only the most recent year due to year-to-year variability – with the following groups of years:

1) The immediately preceding period of lower concentrations (1994-2006);
2) The period of higher concentrations (1988-1992); and
3) The earlier period of intermediate concentrations (1984-1986).

These contrasts were done for TPCB concentrations for smallmouth bass for each of the four stations and for brown trout from West Cornwall. CTPCB was not calculated until 1992, so the last two contrasts could not be done for CTPCB (although recent years' concentrations were compared to those from 1992). There were no smallmouth bass from Lake Zoar in 1986, so the contrasts for TPCB at Lake Zoar exclude that year from the comparison.

The contrasts were performed using Statistica software.

Results

Smallmouth bass

Concentrations of TPCB in smallmouth bass in the three most recent years (2006-2010) were not significantly different from concentrations in the 1994-2004 period at all stations except Lake Zoar, where they were significantly higher in recent years (Table L-1). Concentrations in recent years were also not significantly different from concentrations in 1984-1986 at West Cornwall and Lake Zoar, but were significantly lower than concentrations in 1984-1986 at Bulls Bridge and Lake Lillinonah. Concentrations in recent years were significantly lower than concentrations in 1988-1992 at all stations.

Concentrations of CTPCB in smallmouth bass in the recent years were not significantly different from concentrations in 1994-2004 at West Cornwall and Bulls Bridge, were significantly lower than those in 1994-2004 at Lake Lillinonah, and were significantly higher than those in 1994-2004 at Lake Zoar (Table L-1). CTPCB concentrations in recent years were significantly lower than concentrations in 1992 at all stations except Lake Zoar, where there was no significant difference.

Table L-1. Results of smallmouth bass linear contrasts of recent years (2006-2010) with other year groups representing periods of intermediate concentrations (1984-1986), high concentrations (1988-1992 for TPCB or 1992 for CTPCB), and low concentrations (1994-2004). Significance was at p=0.05.

Comparison Group	Station				
TPCB	**C**	**B**	**L**	**Z**	**All Stations**
1984-1986	ns	0.02698	<0.00001	ns	<0.00001
1988-1992	<0.00001	<0.00001	<0.00001	0.001180	<0.00001
1994-2004	ns	ns	ns	0.035970	ns
CTPCB					
1992	<0.00001	0.001980	0.000340	ns	<0.00001
1994-2004	ns	ns	0.038920	0.006600	ns

Brown trout

Brown trout concentrations of TPCB in the recent years (2006-2010) were not significantly different from those in 1994-2004, but were significantly lower than concentrations in 1984-1986 and 1988-1992 (Table L-2).

Similarly, brown trout concentrations of CTPCB in the recent years were not significantly different from those in 1994-2004, but were significantly lower than concentrations in 1992 (Table L-2).

Table L-2. Results of brown trout linear contrasts of recent years (2010, 2008, 2006) with other year groups representing periods of intermediate concentrations (1984-1986), high concentrations (1988-1992 for TPCB or 1992 for CTPCB), and the preceding period of low concentration (1994-2004). Significance was at p=0.05.

Comparison Group	C
TPCB	
1984-1986	<0.00001
1988-1992	<0.00001
1994-2004	ns
CTPCB	
1992	<0.00001
1994-2004	ns